

FIG. 1A

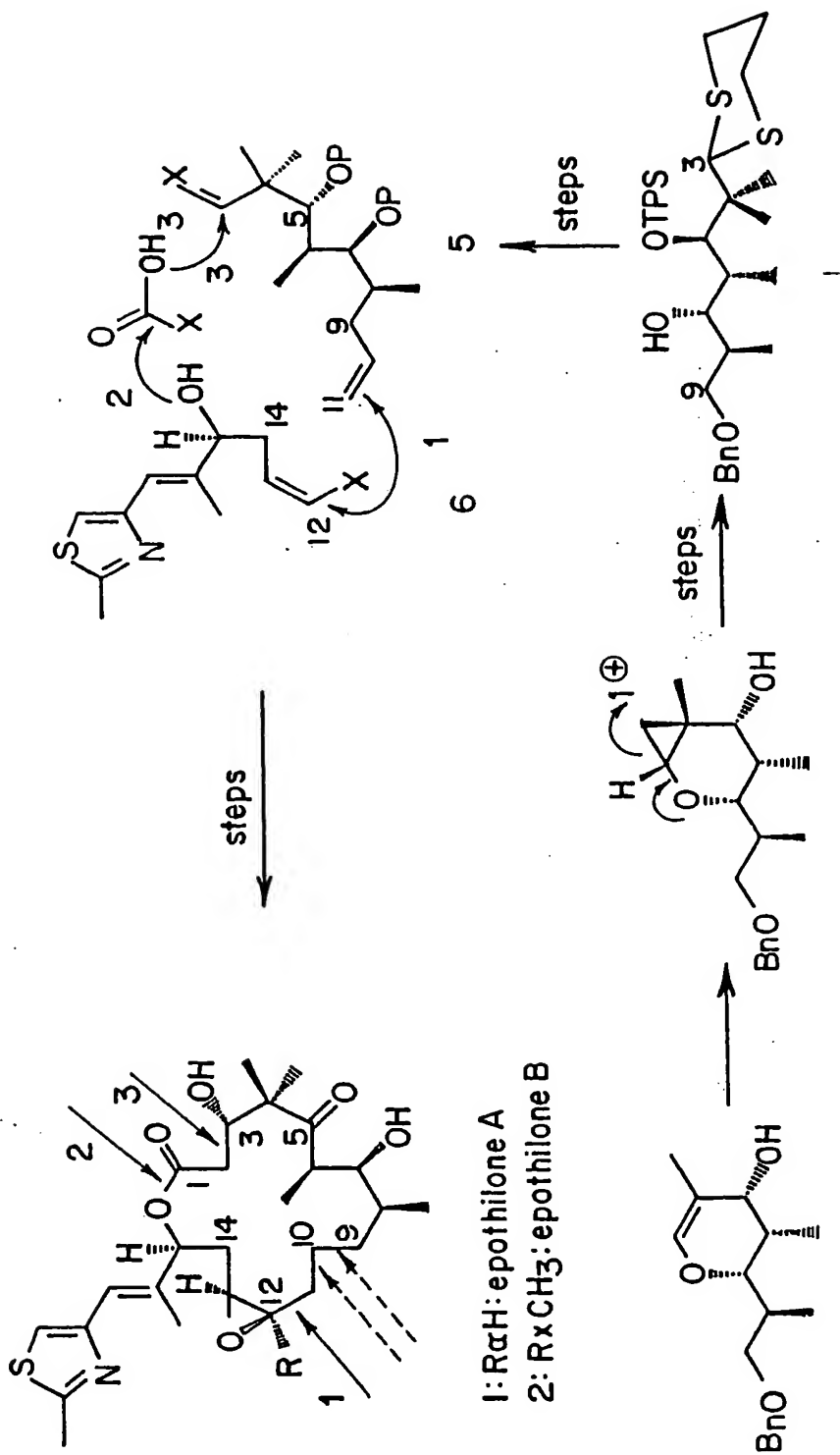


FIG. 1B

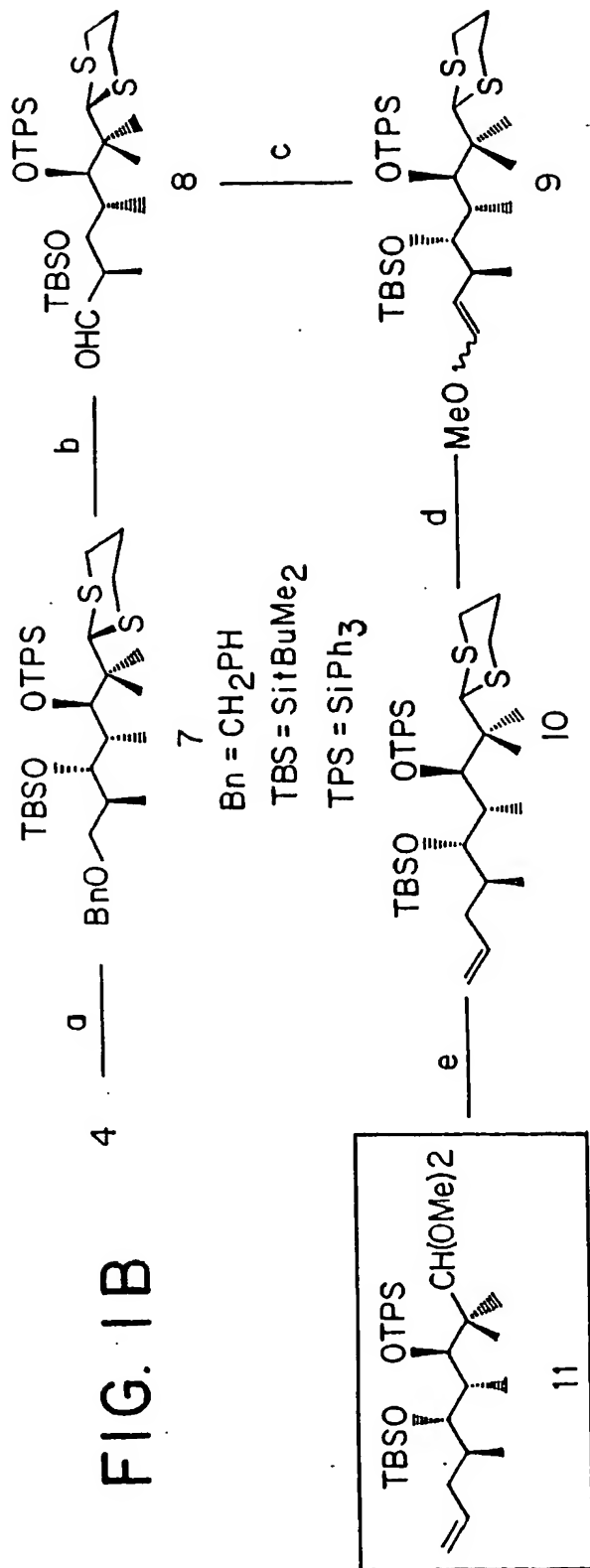


FIG. 12B

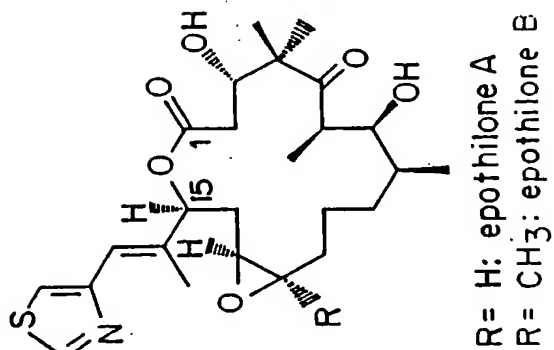
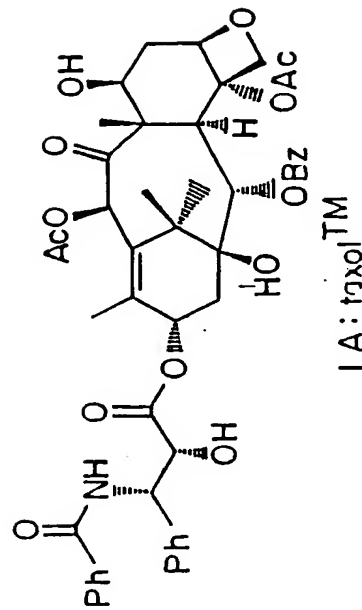
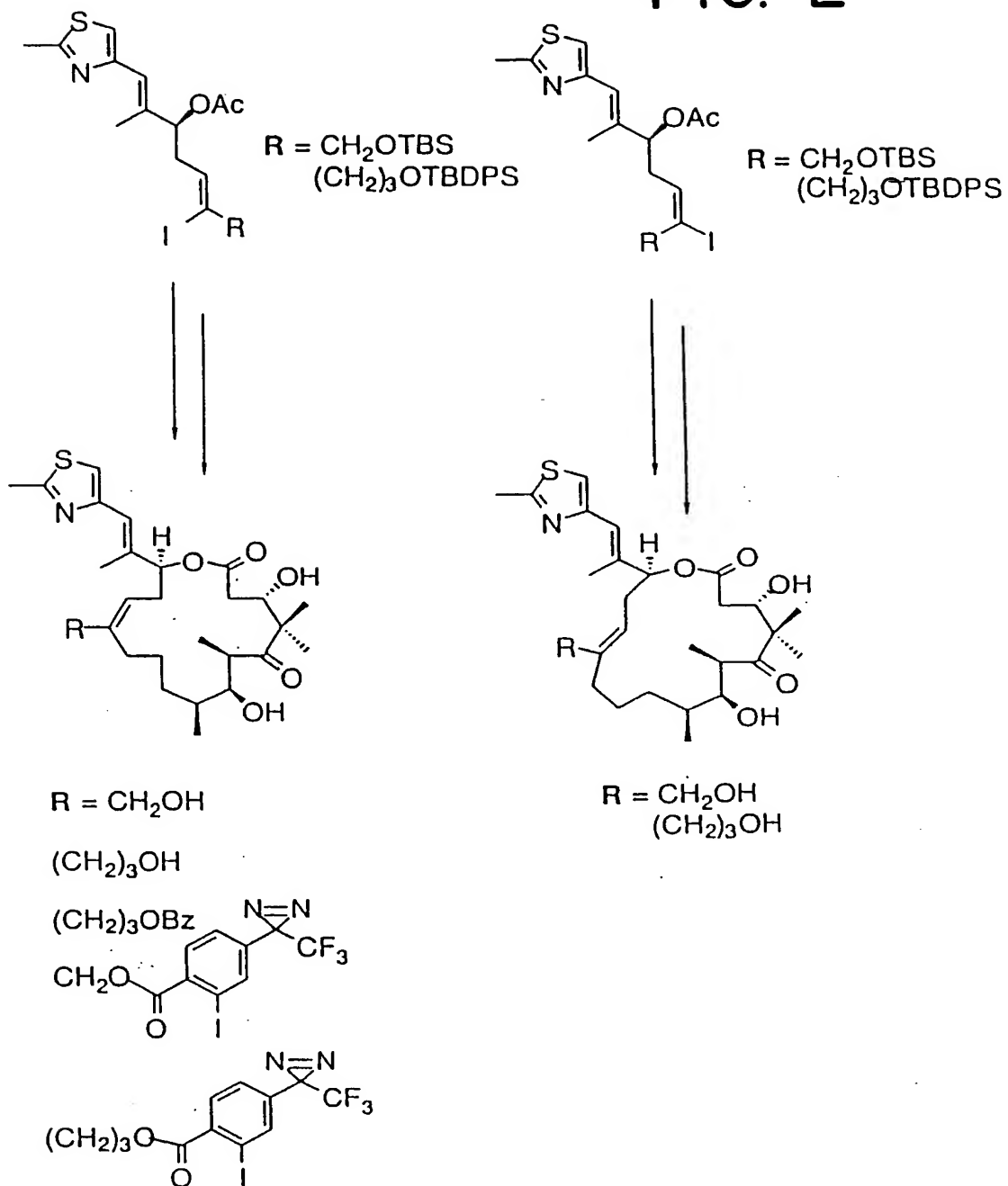


FIG. 12A

FIG. 2



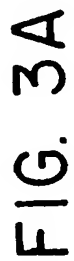
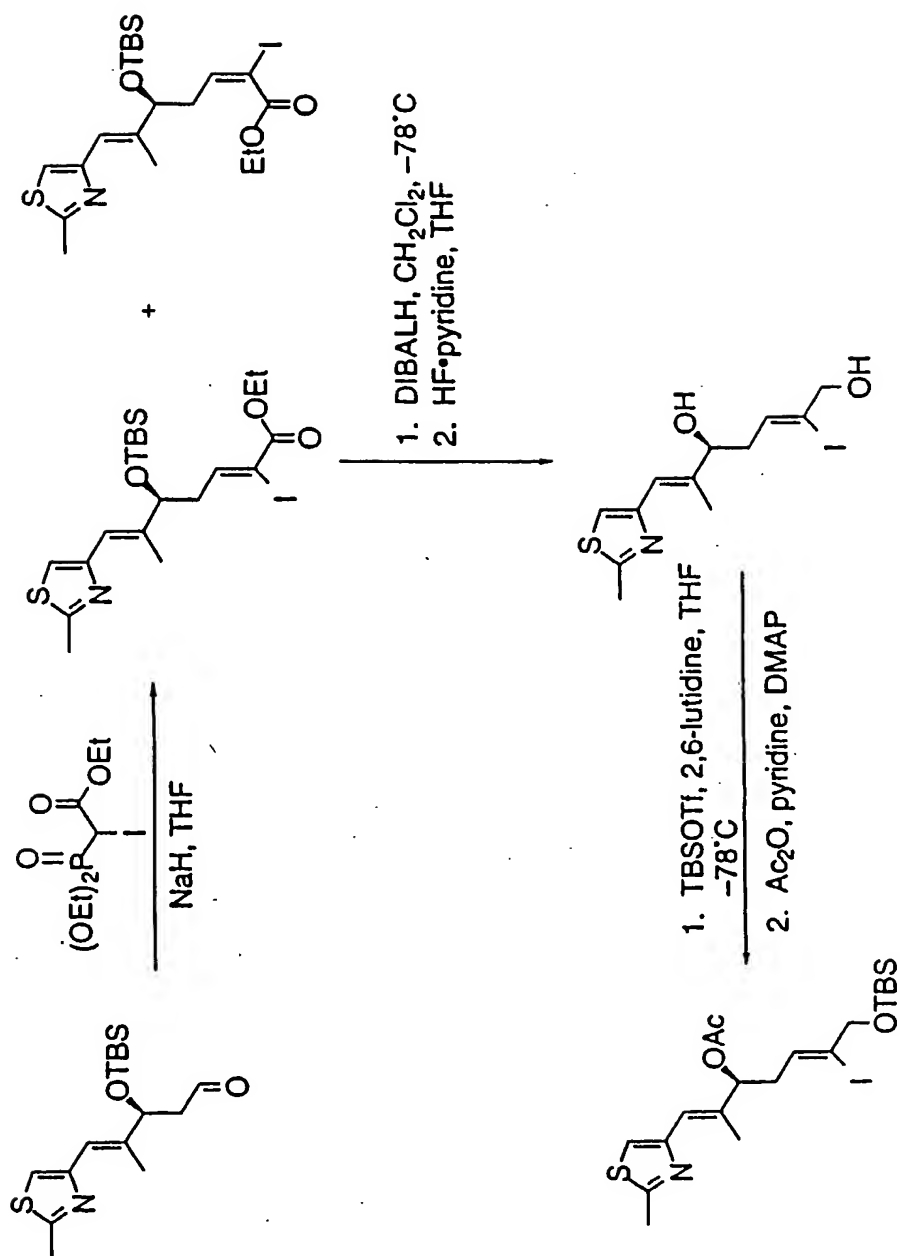


FIG. 3B



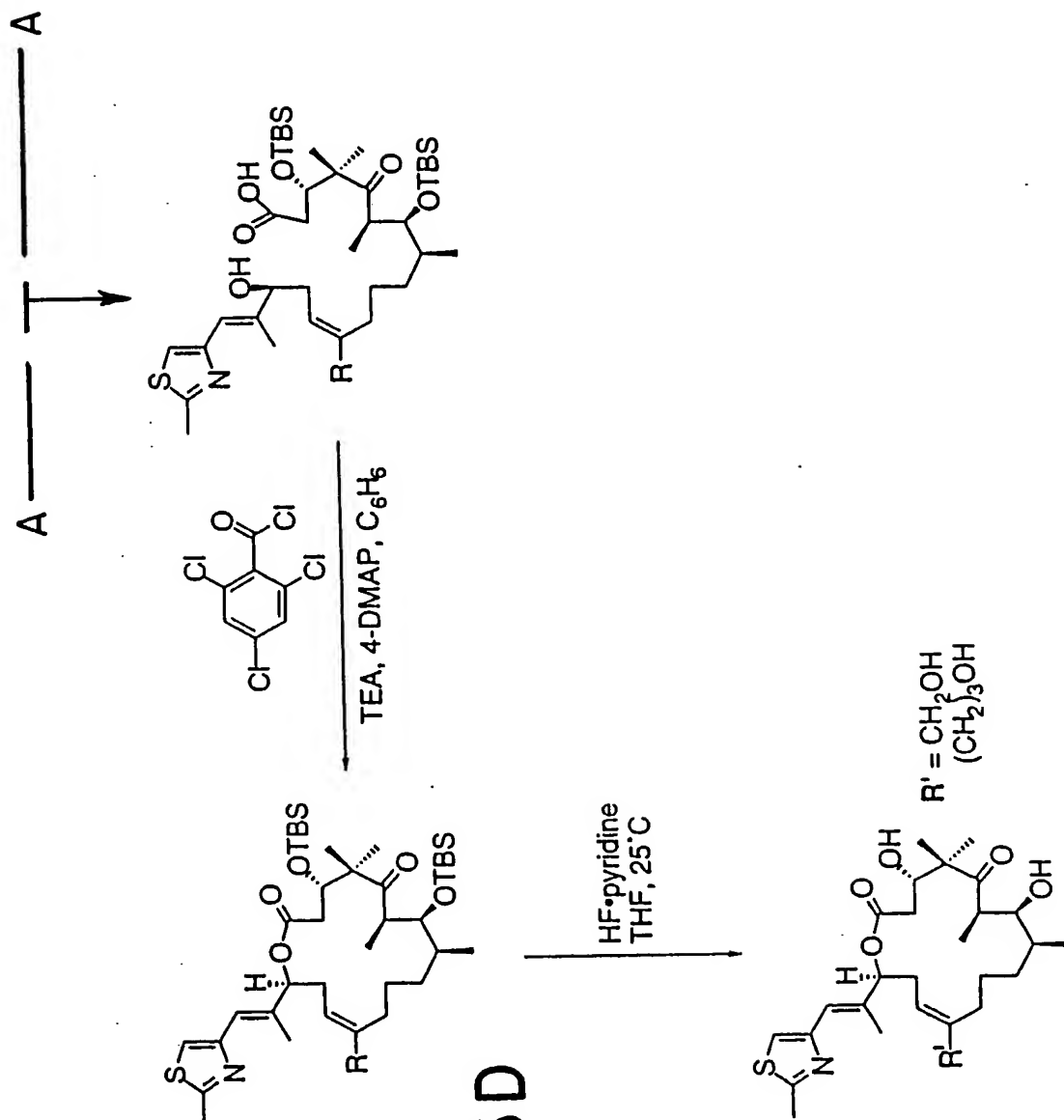


FIG. 3D

FIG. 3E

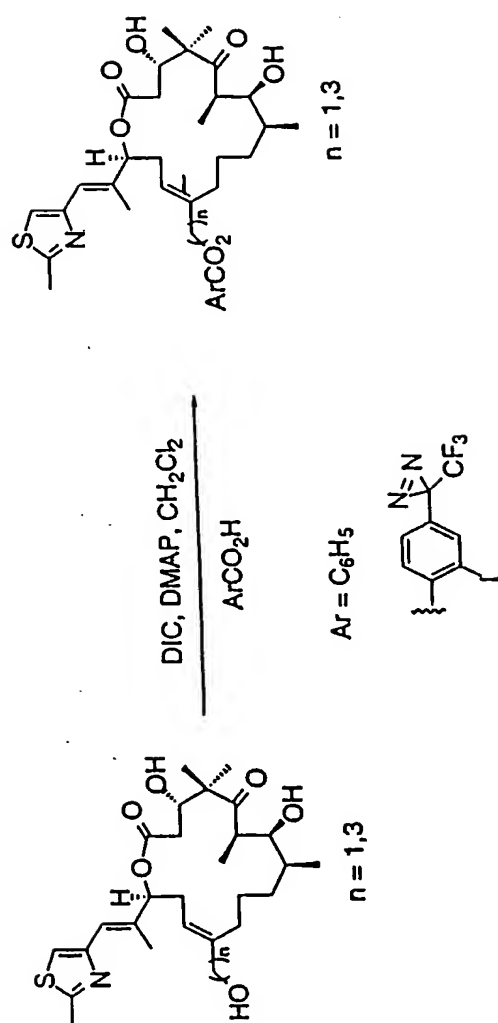


FIG. 3F

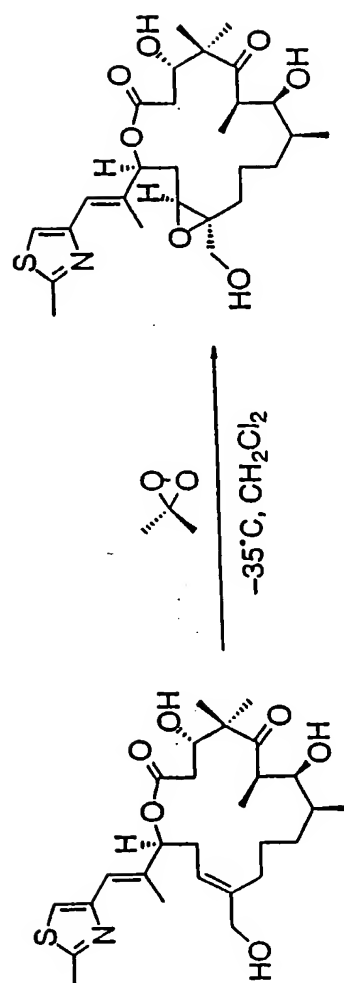


FIG. 4A

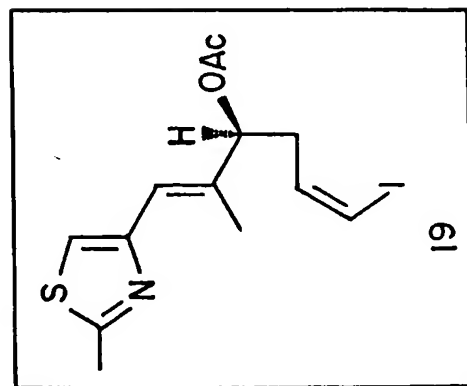
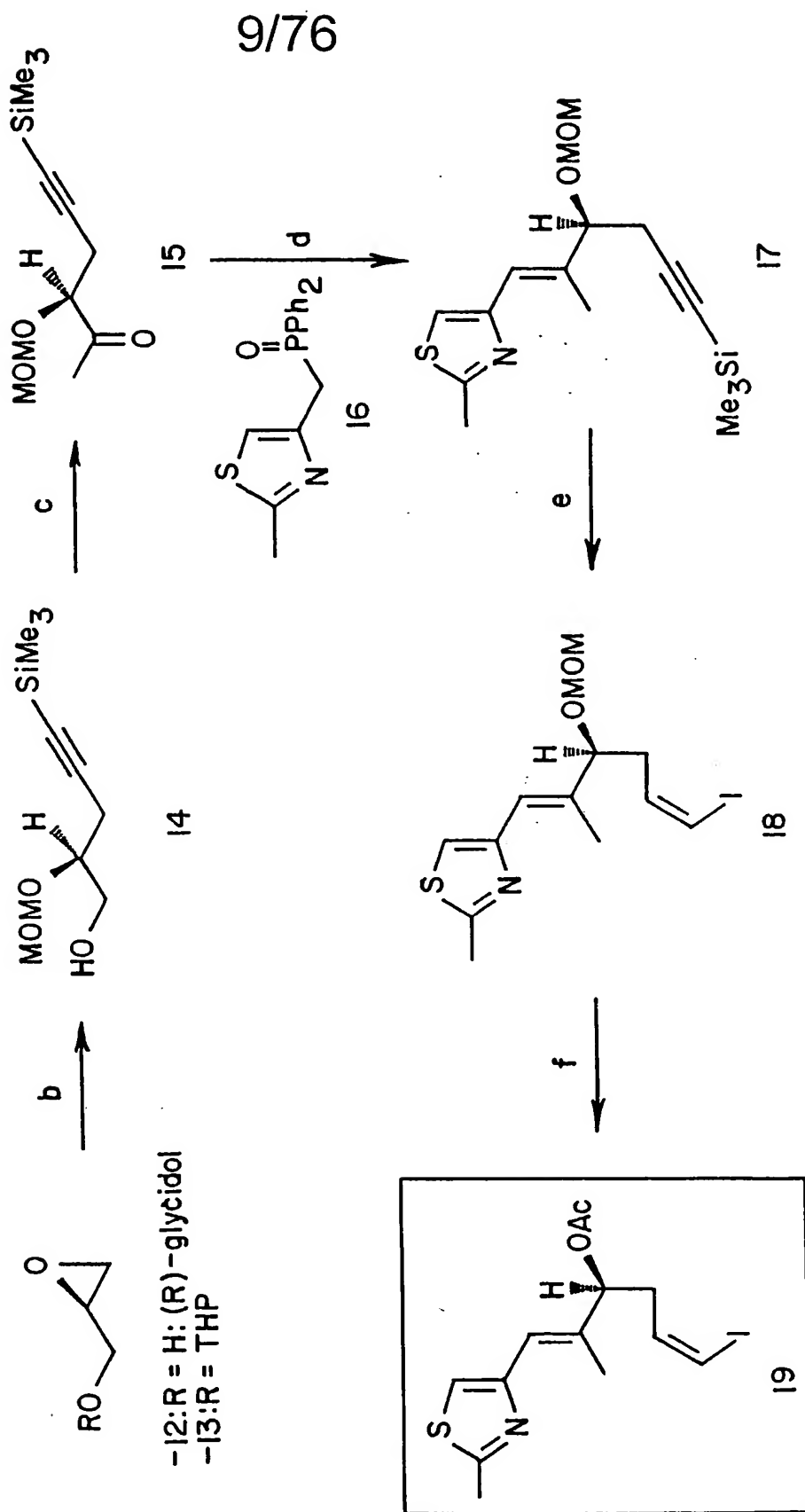


FIG. 4B

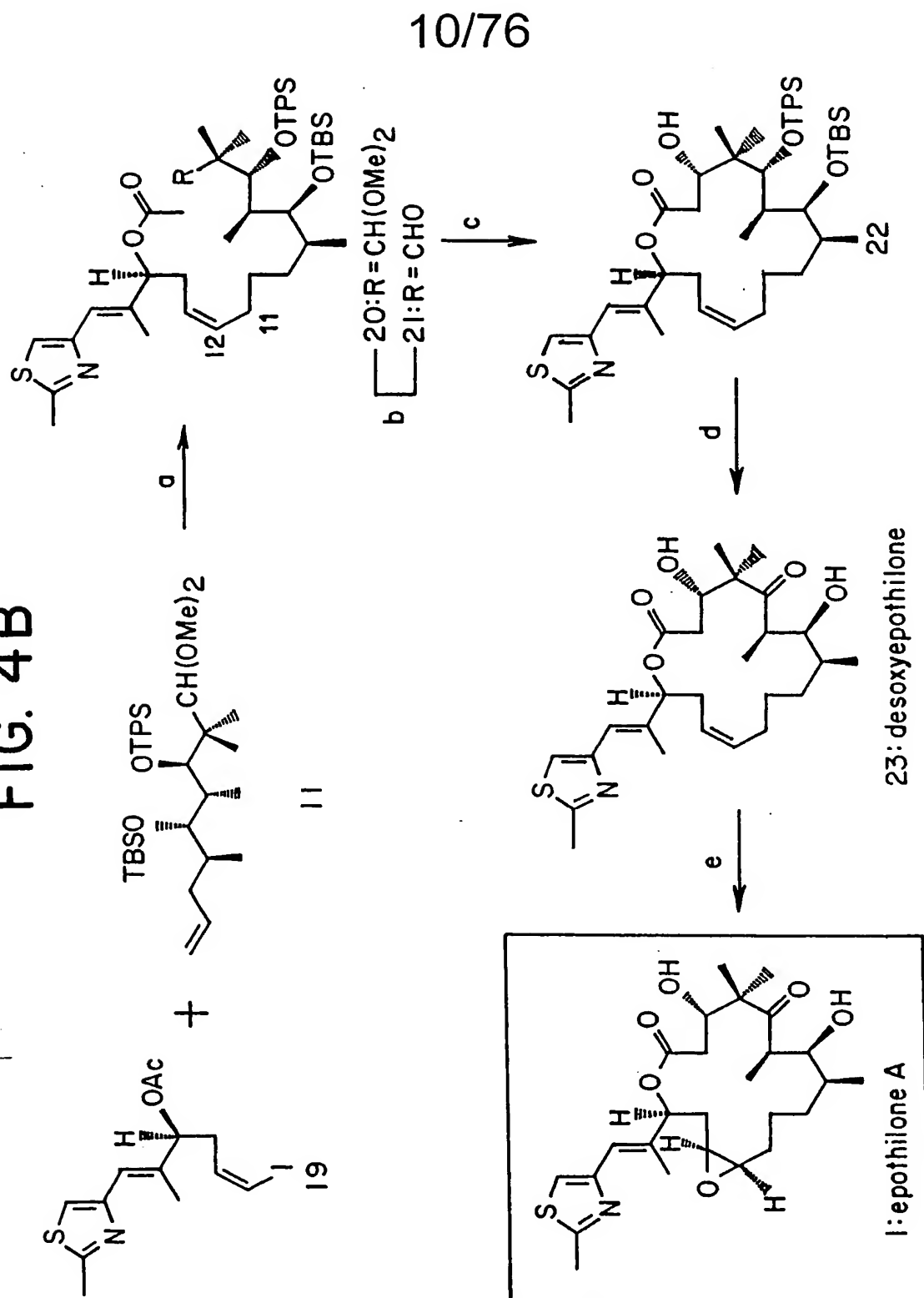


FIG. 5

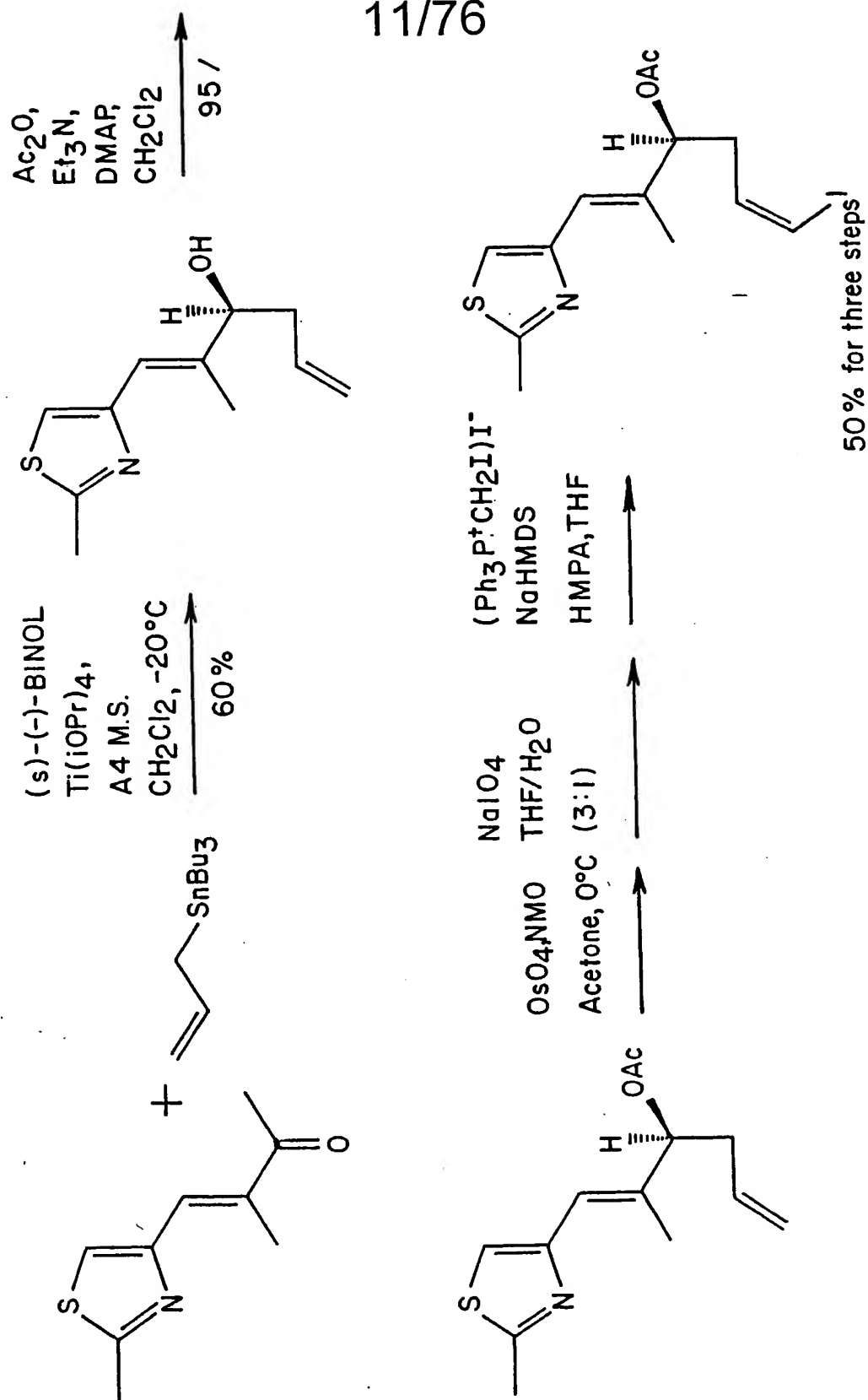


FIG. 6A

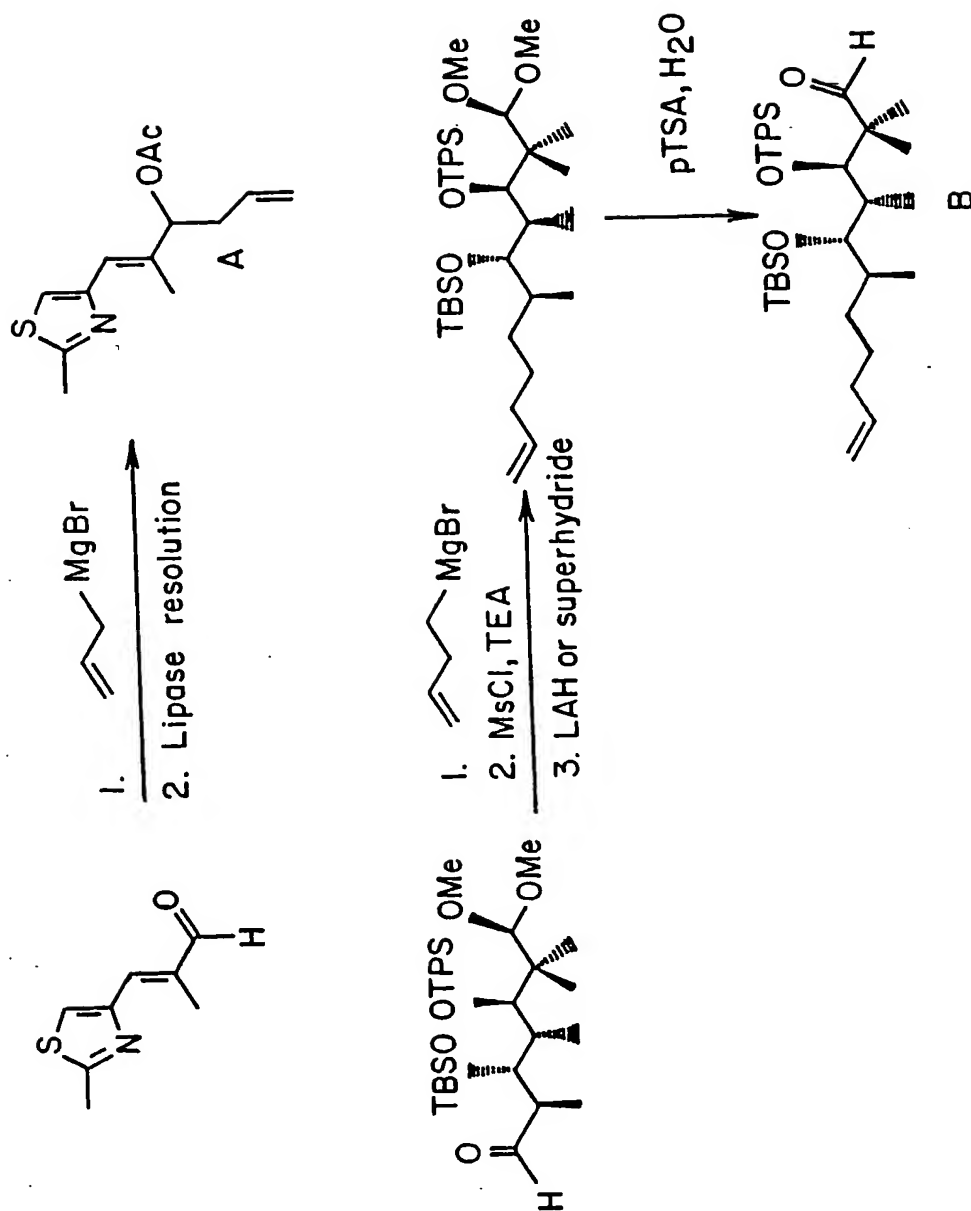
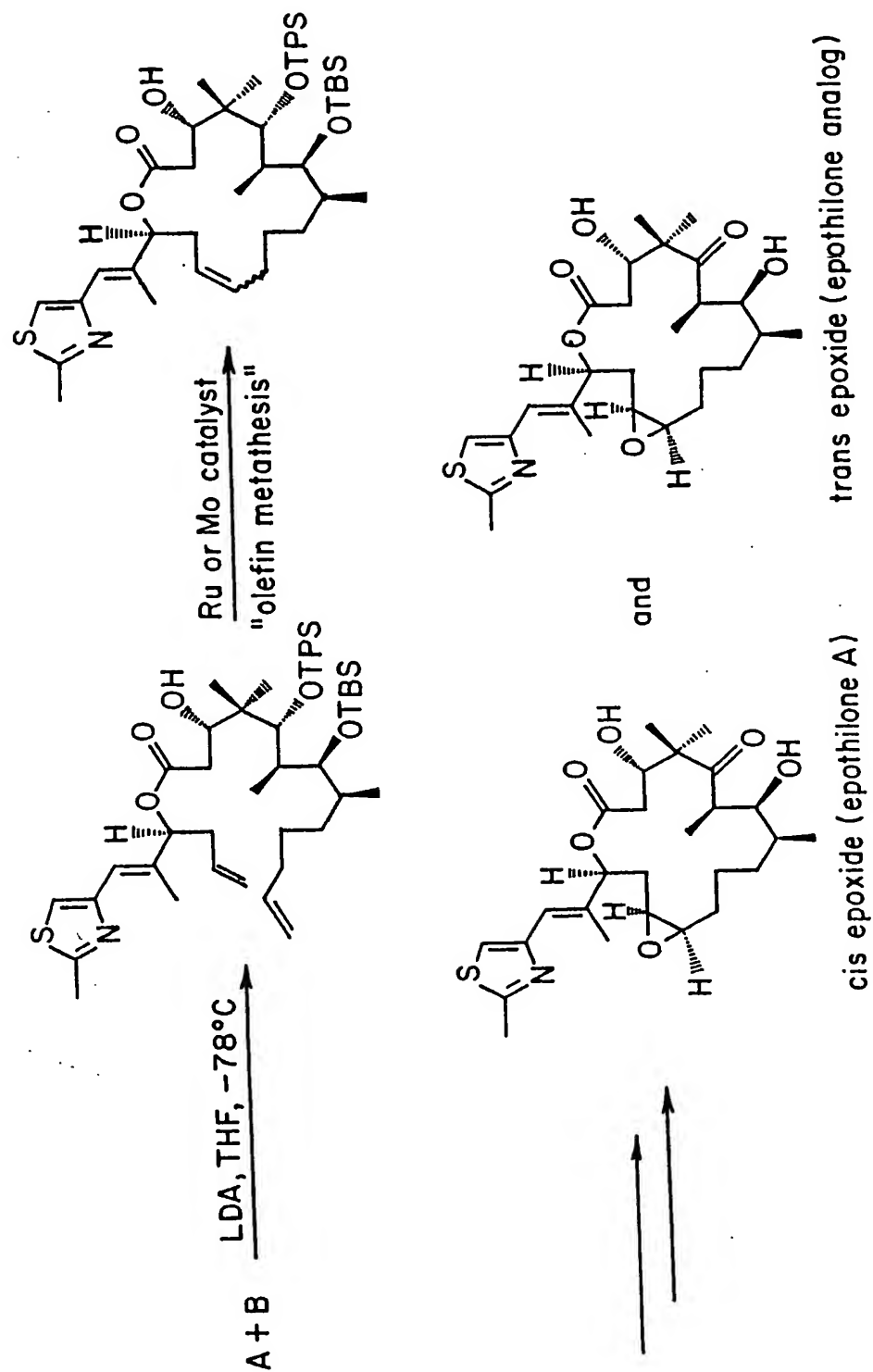
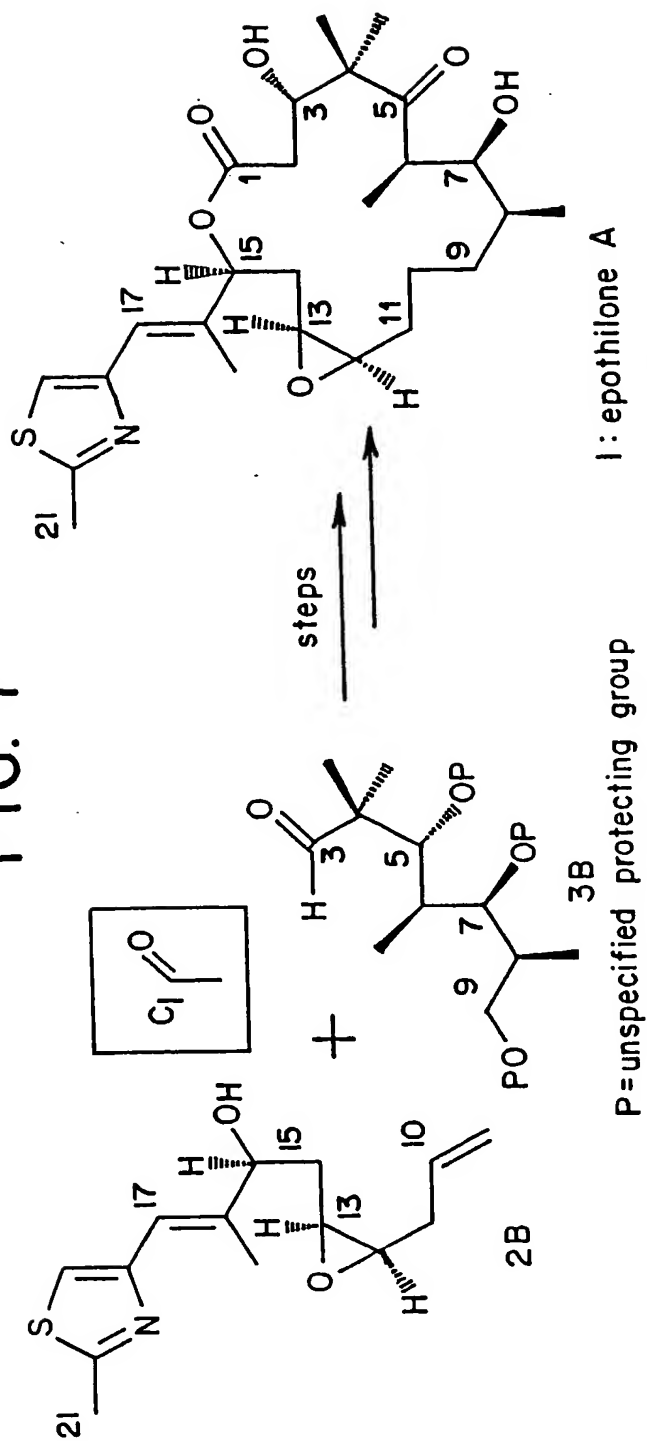


FIG. 6B

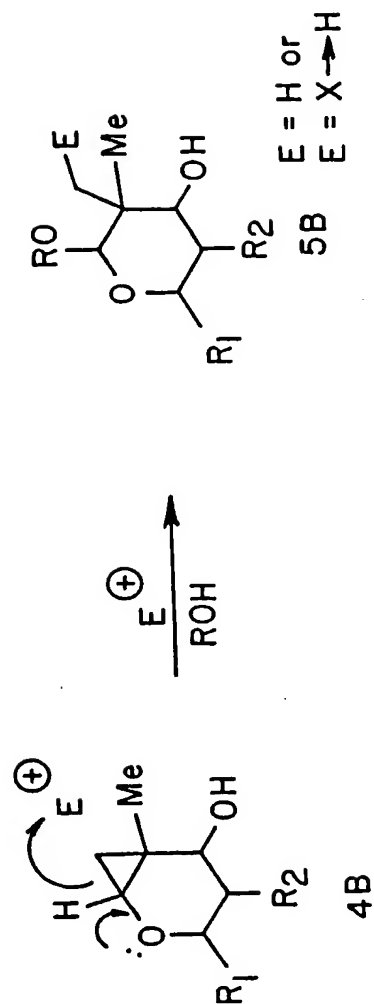


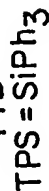
*17 steps from known starting materials vs. 27 steps for aldol macrocyclization

FIG. 7



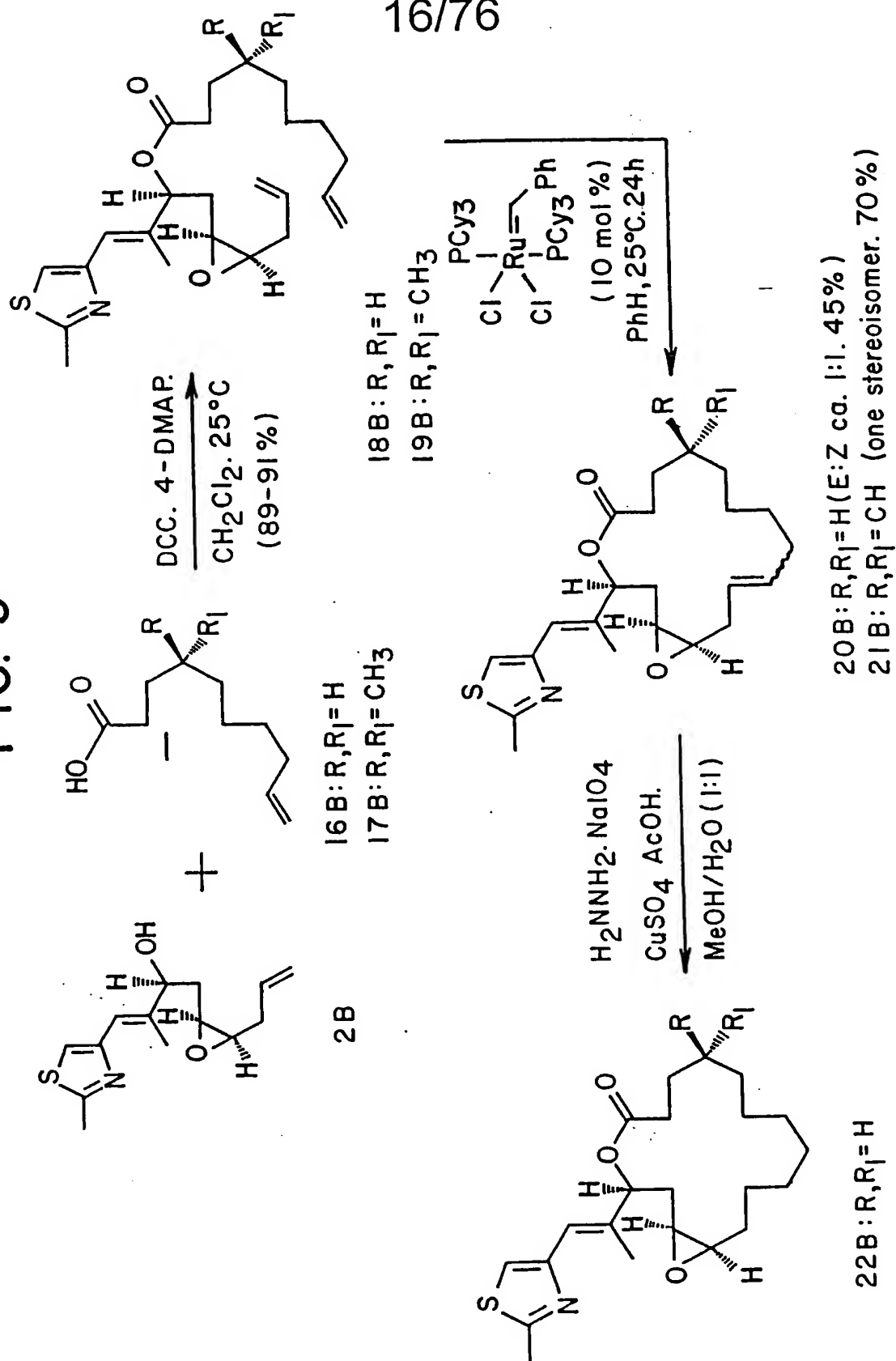
Convergent strategy for a total synthesis of epothilone A (1).





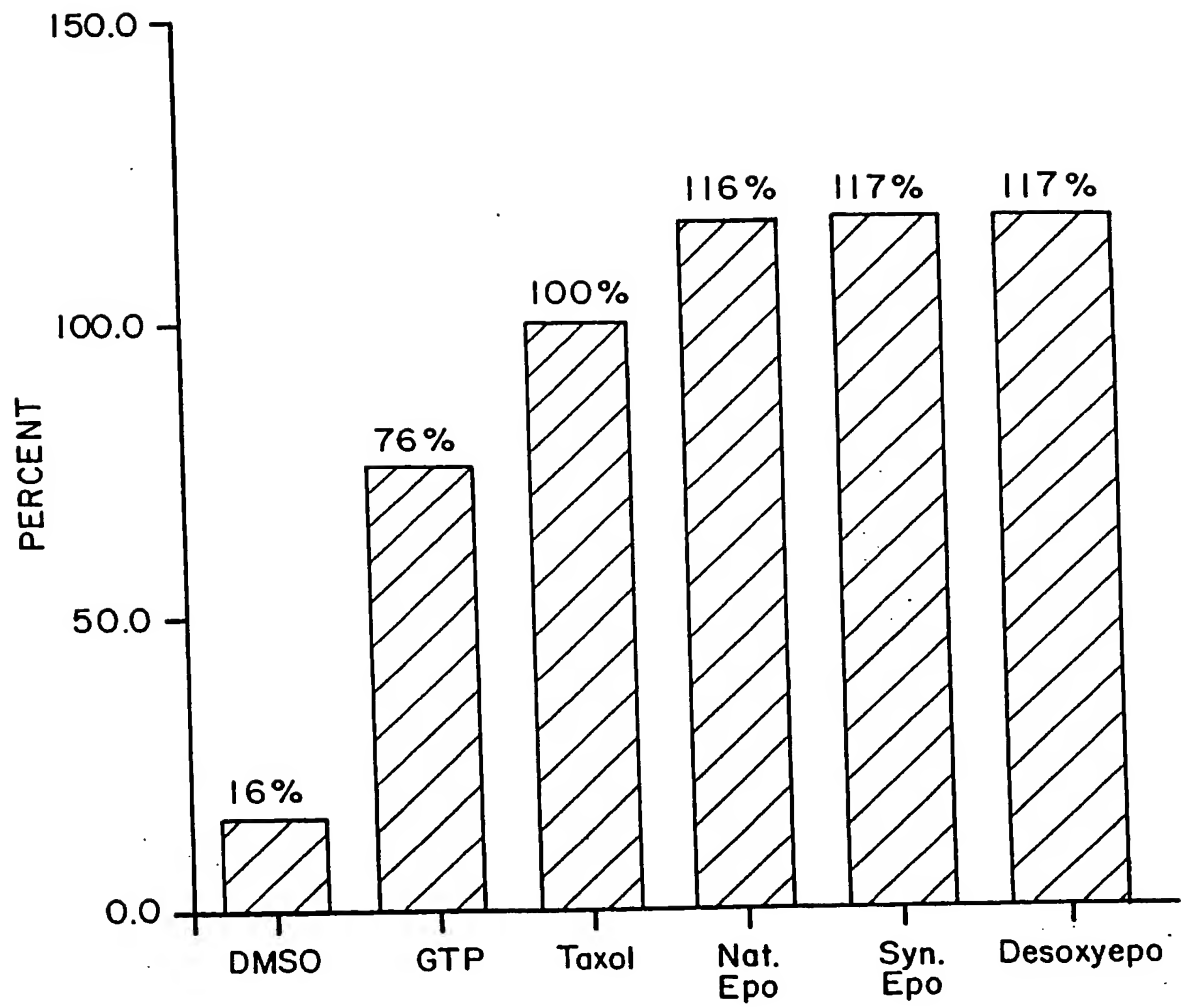
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FIG. 9



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FIG. 10



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FIG. II

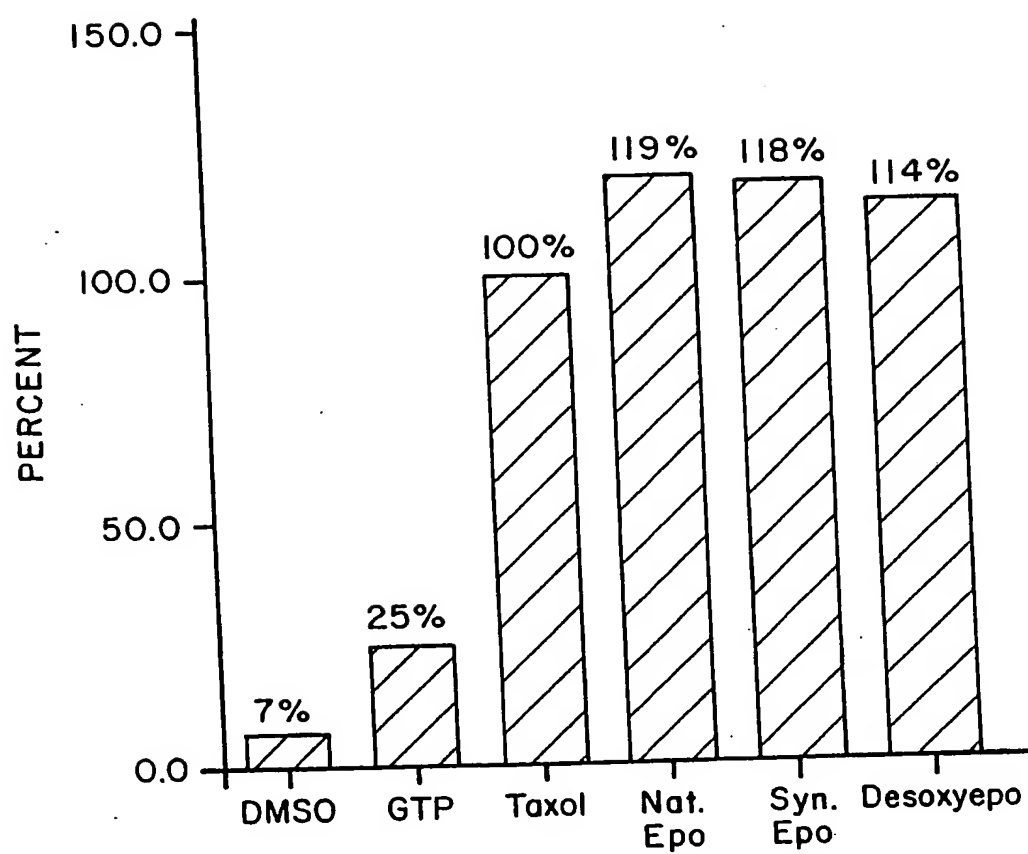


FIG. 13

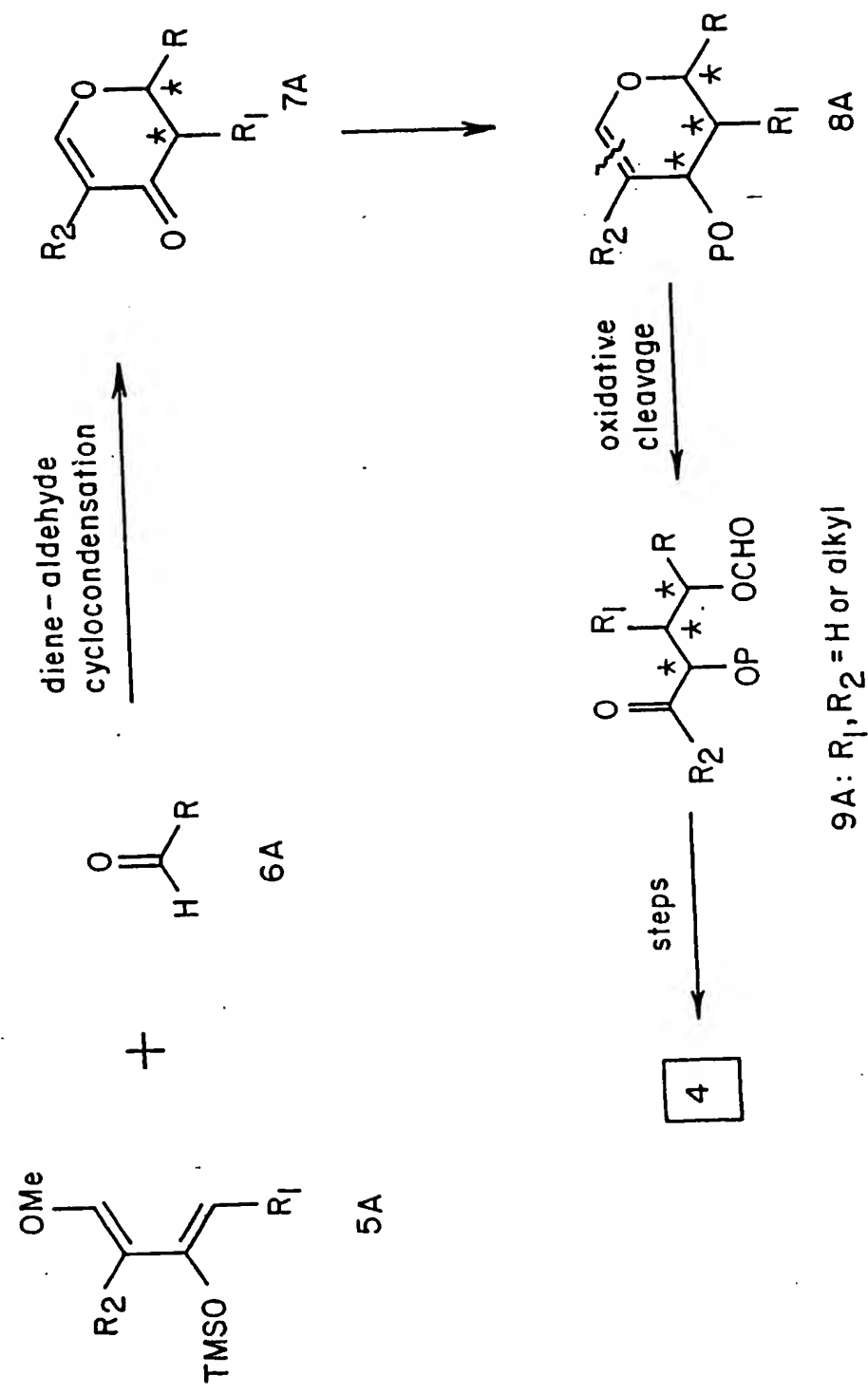


FIG. 14A

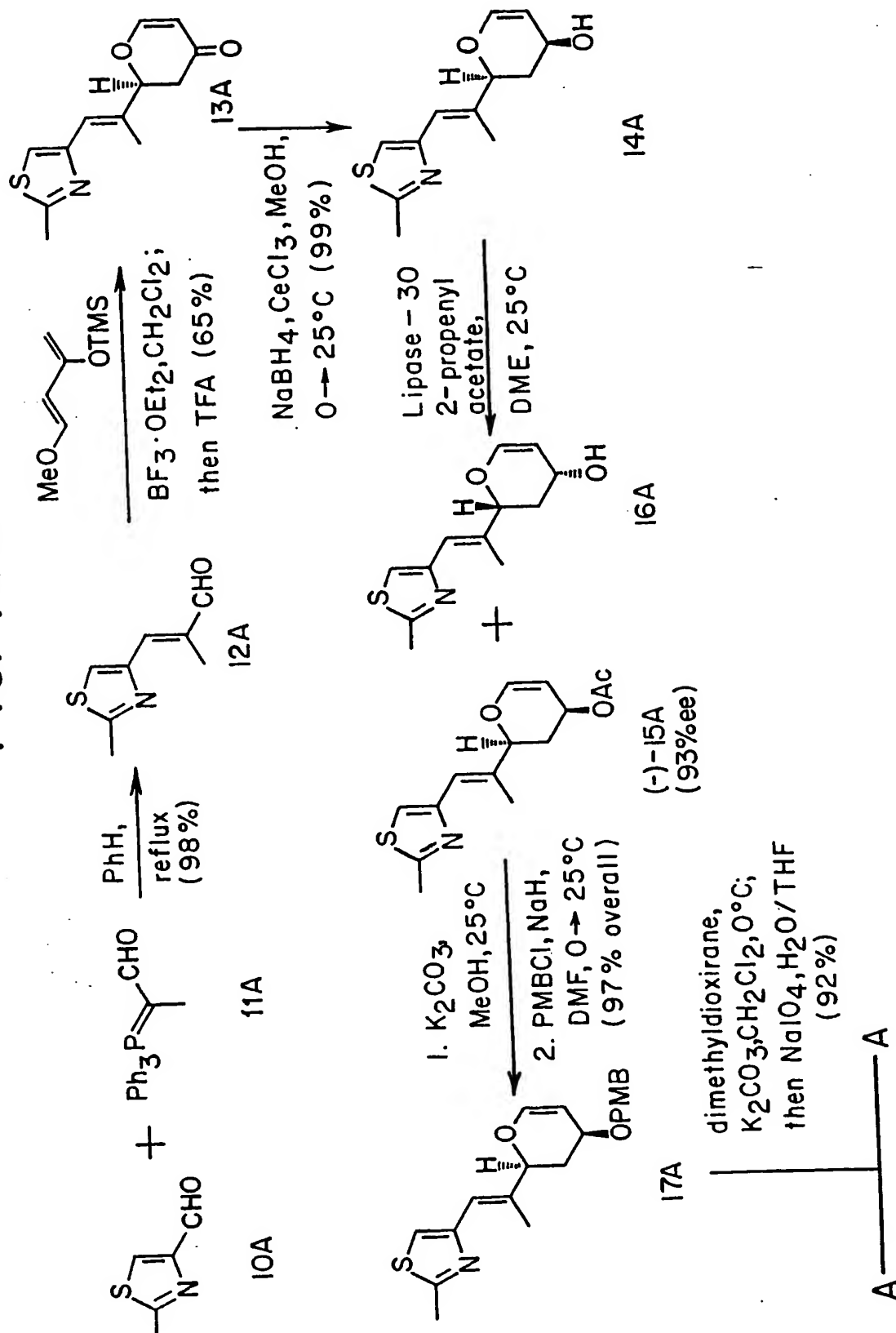
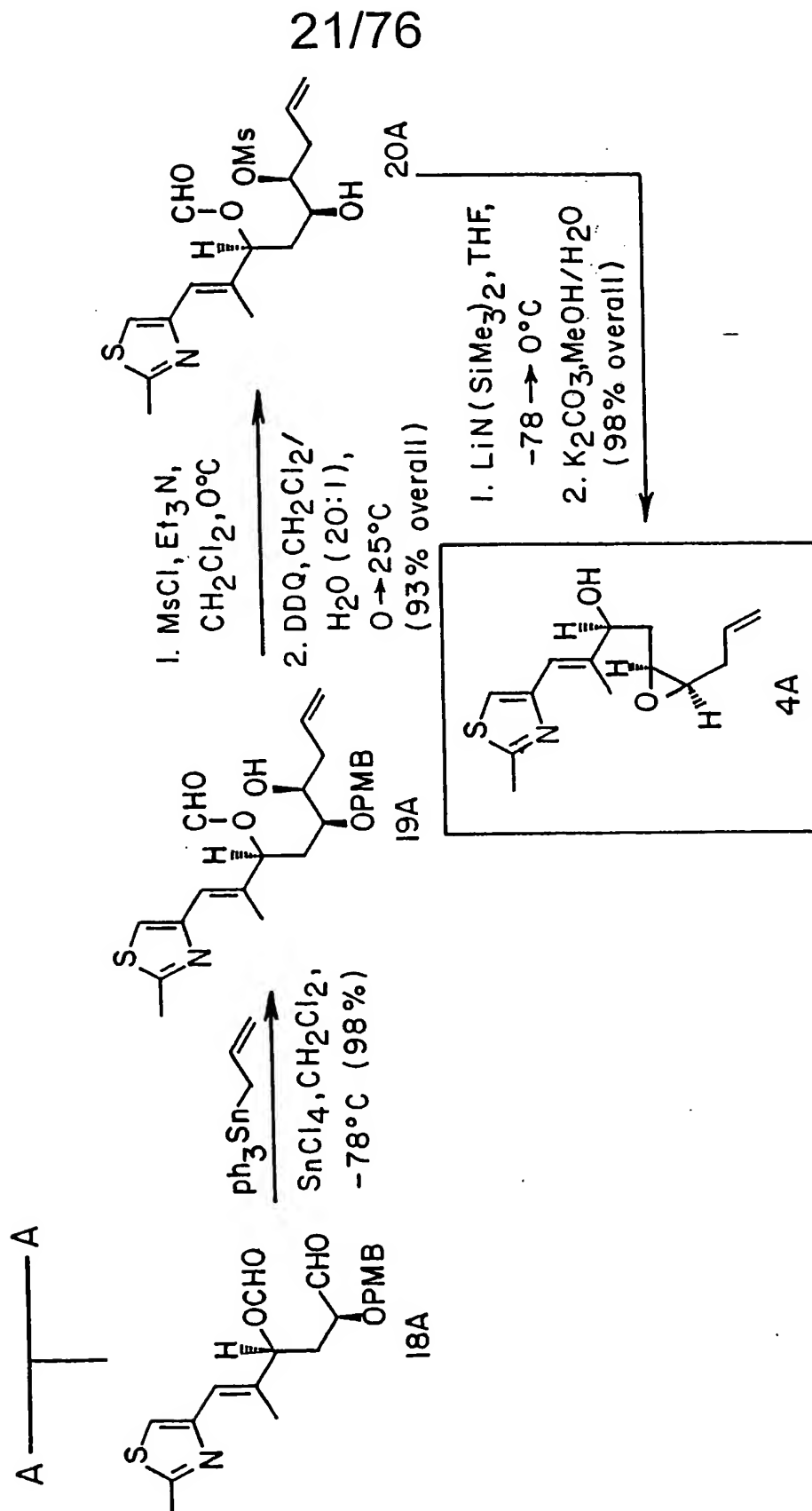



FIG. 14B





CO/C=C/C

OTMS, $\text{MgBr}_2 \cdot \text{OEt}_2$, THF, -10°C , then AcOH, H_2O (93%)

CO[C@H](C)C=O

21A

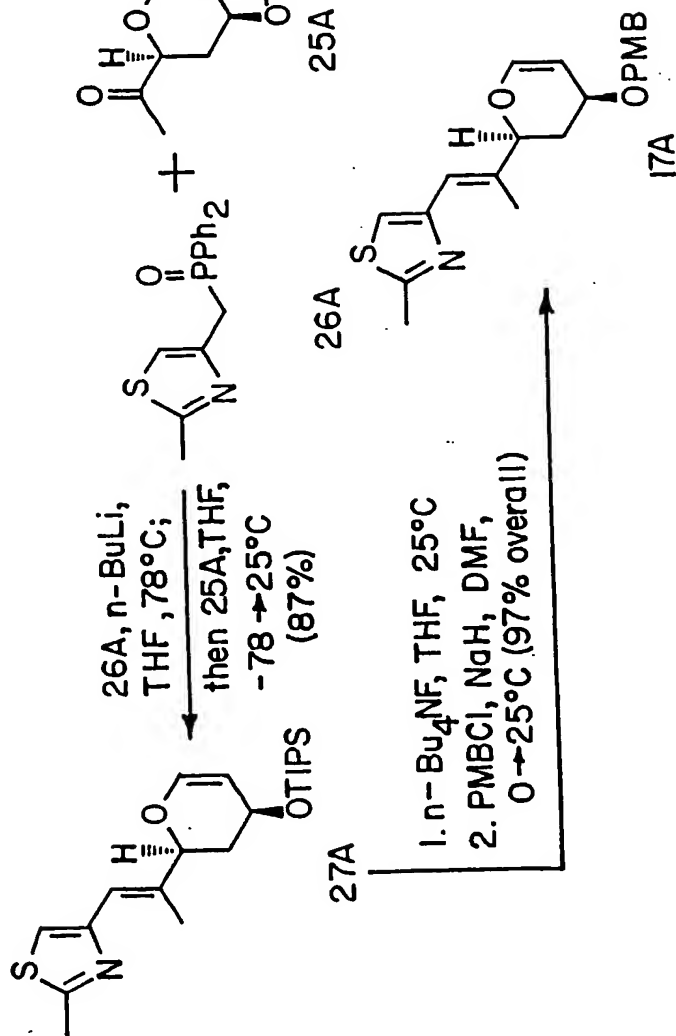


FIG. 16

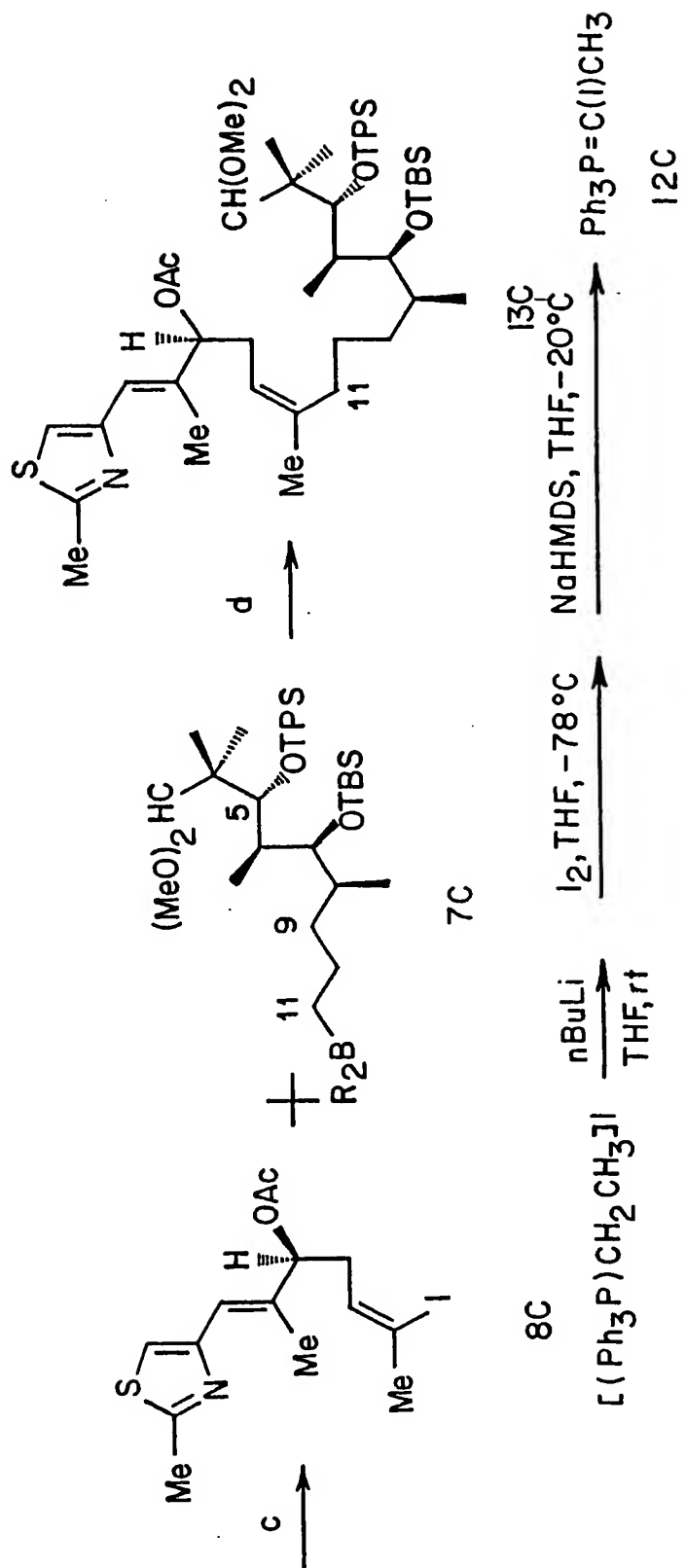
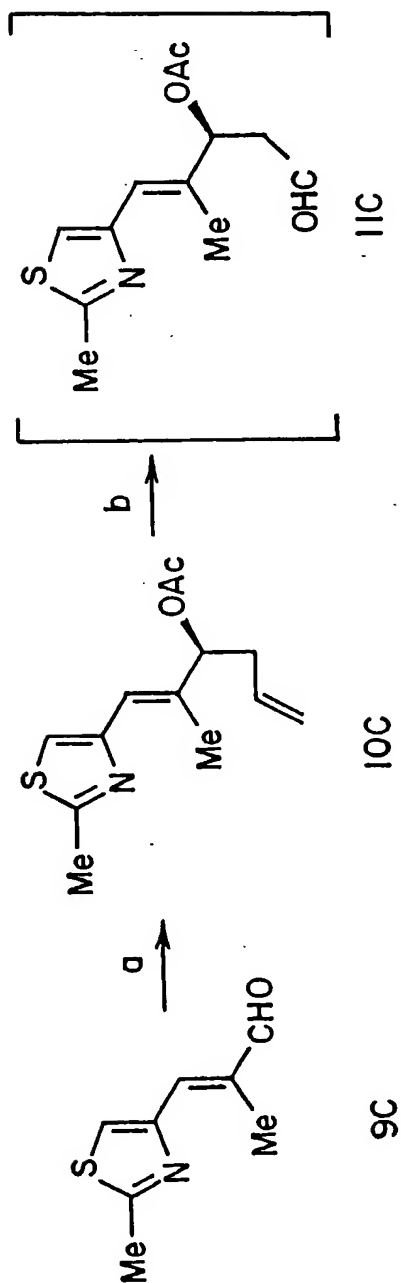
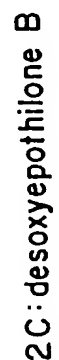


FIG. 17



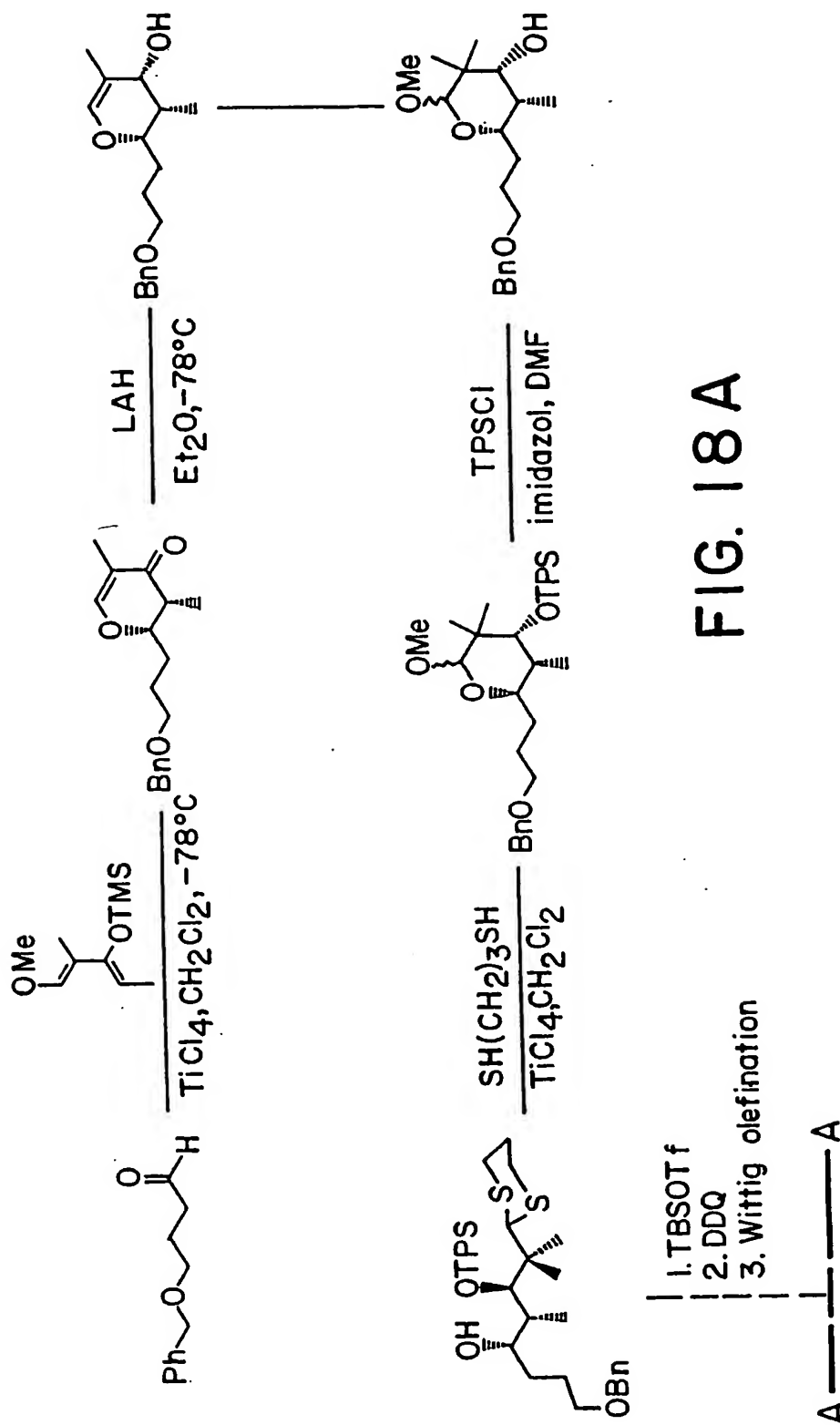


FIG. 18B

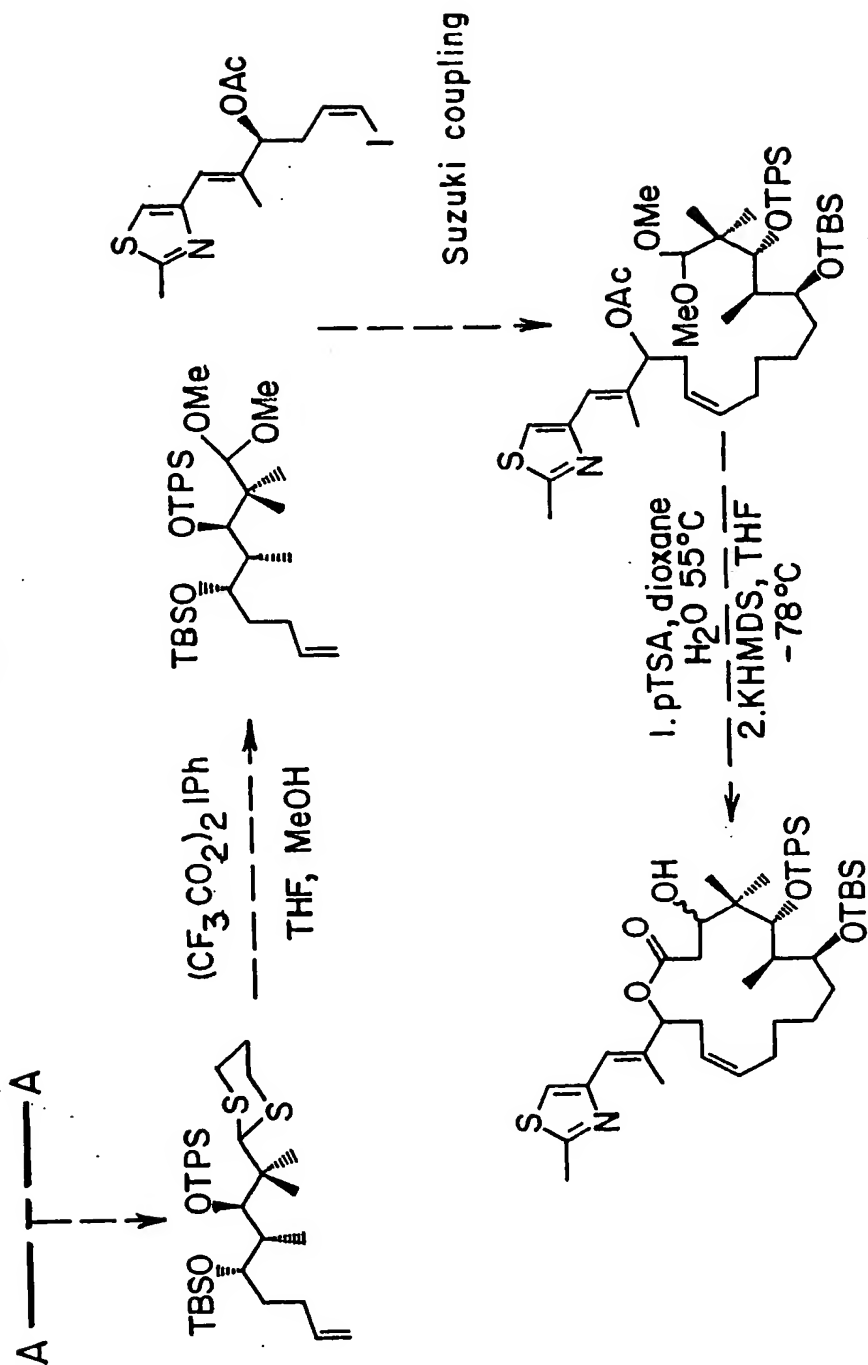


FIG. 19A

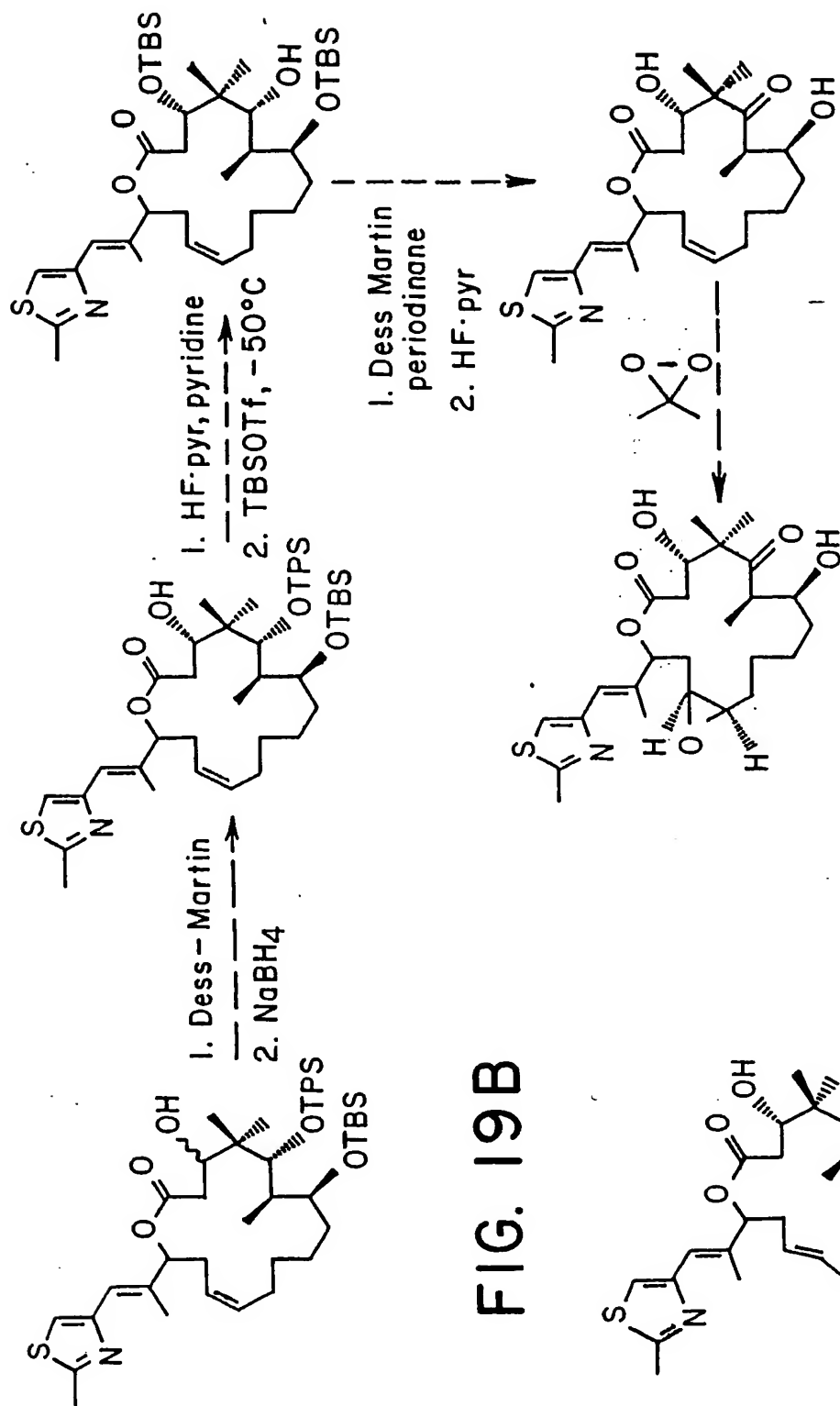
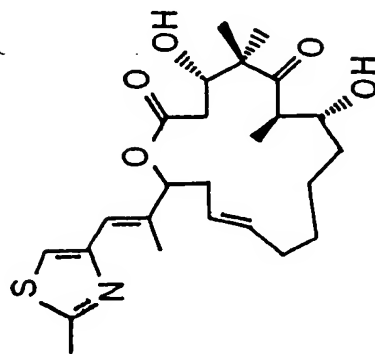


FIG. 19B



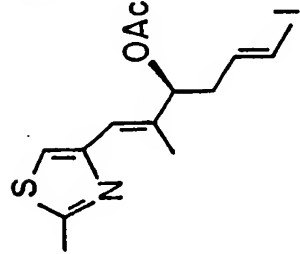


FIG. 19C

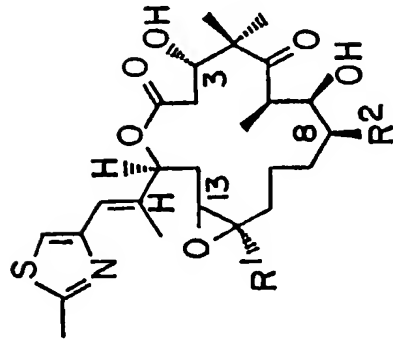


FIG. 20A

R¹ = H, R² = Me; epothilone A

R¹ = R² = Me; epothilone B

R¹ = R² = H; Cg-desmethyl-epothilone A (3D)

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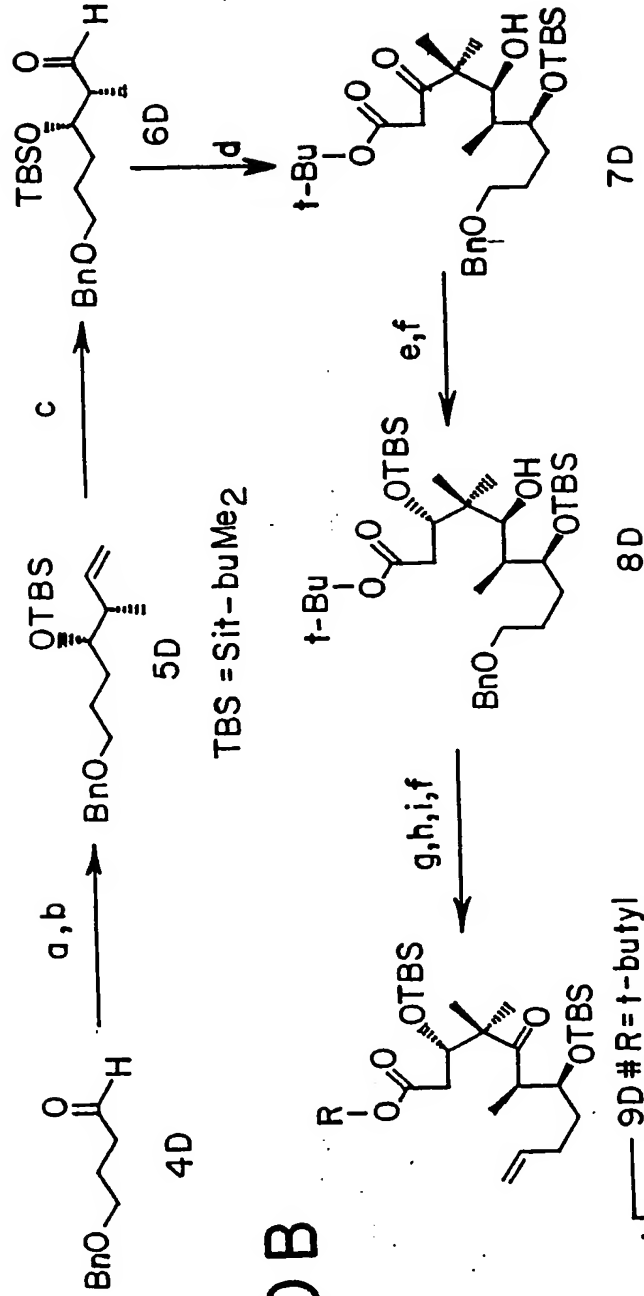


FIG. 20B

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FIG. 21

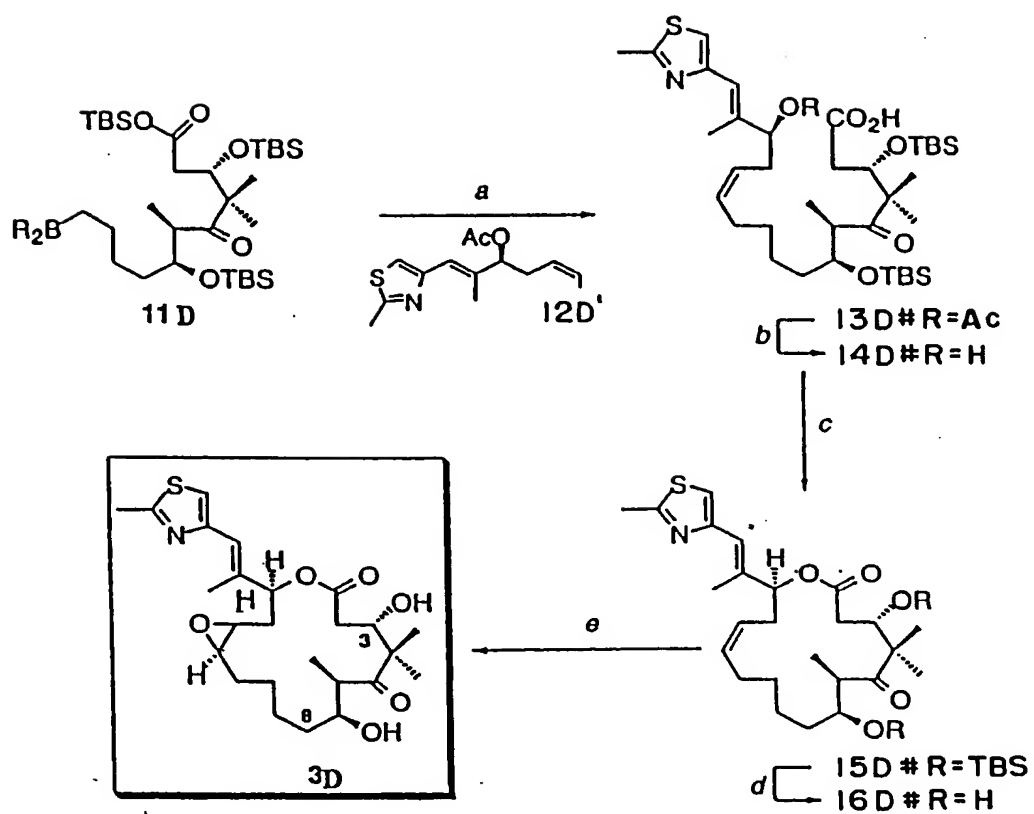


FIG. 22 A

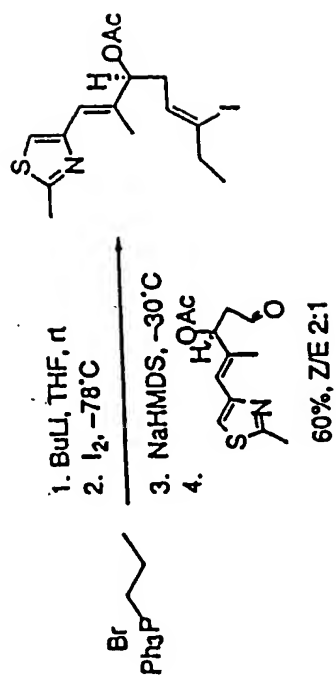


FIG. 22 B

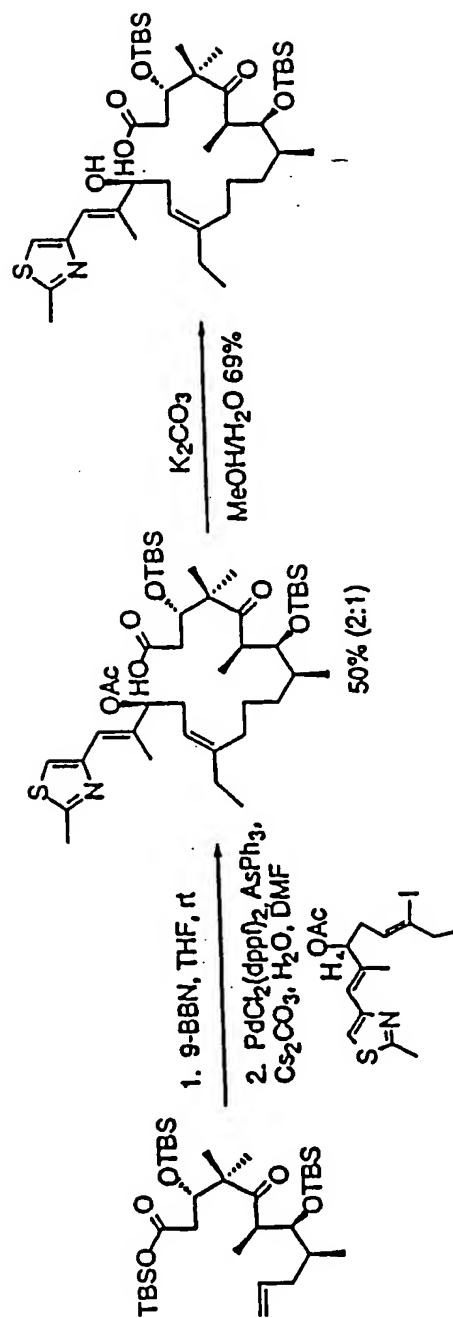


FIG. 22C

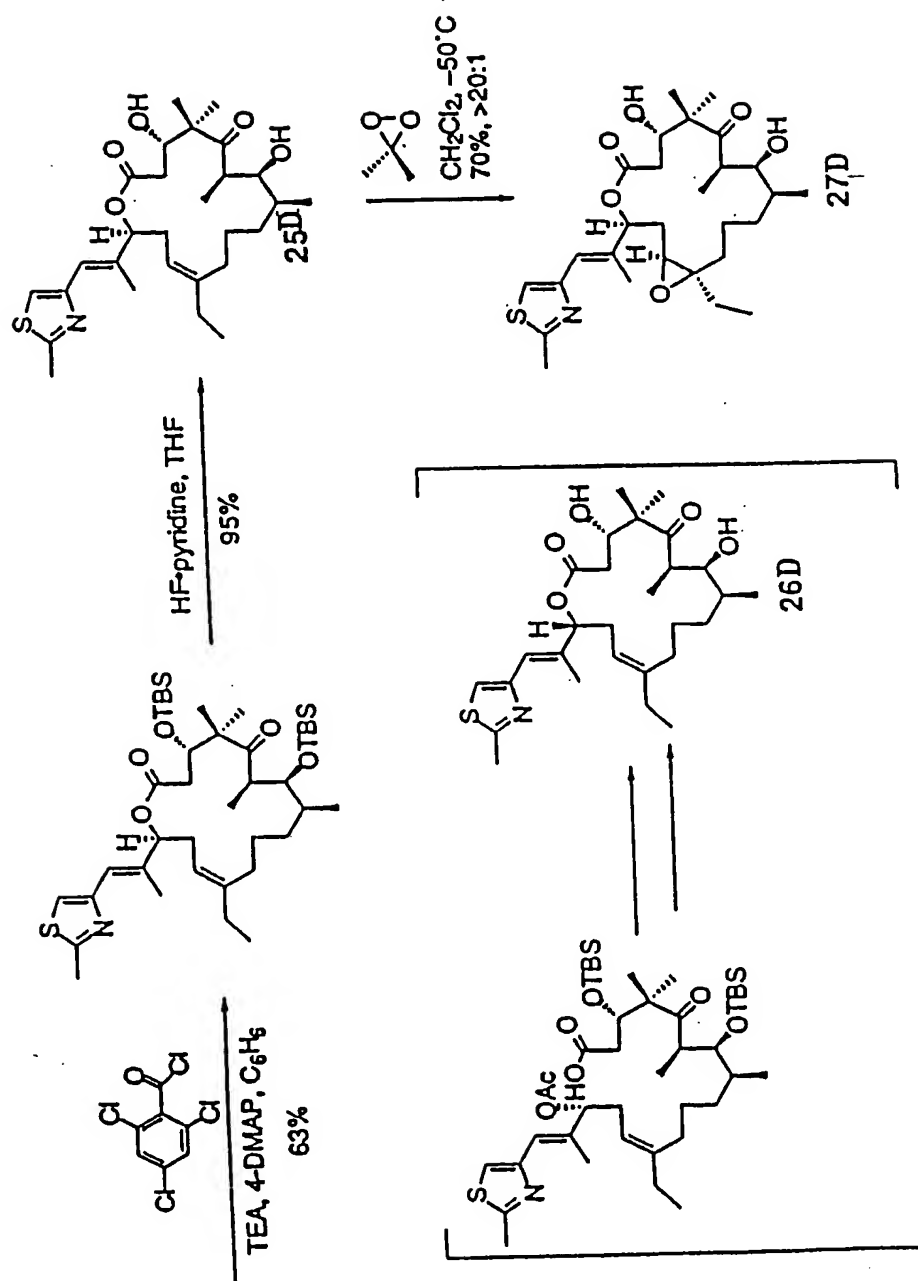


FIG. 23A

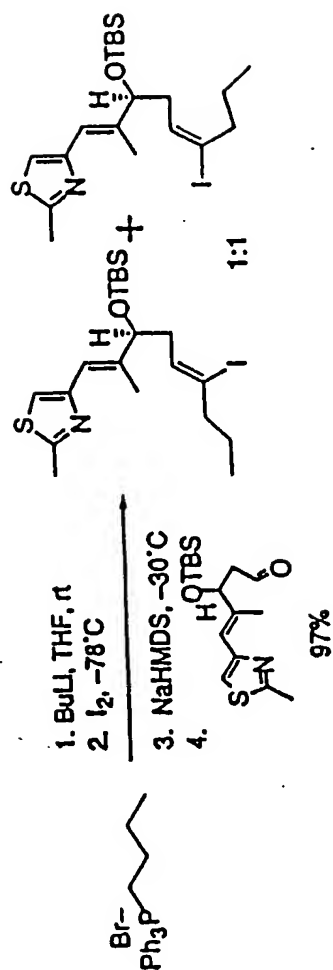


FIG. 23B

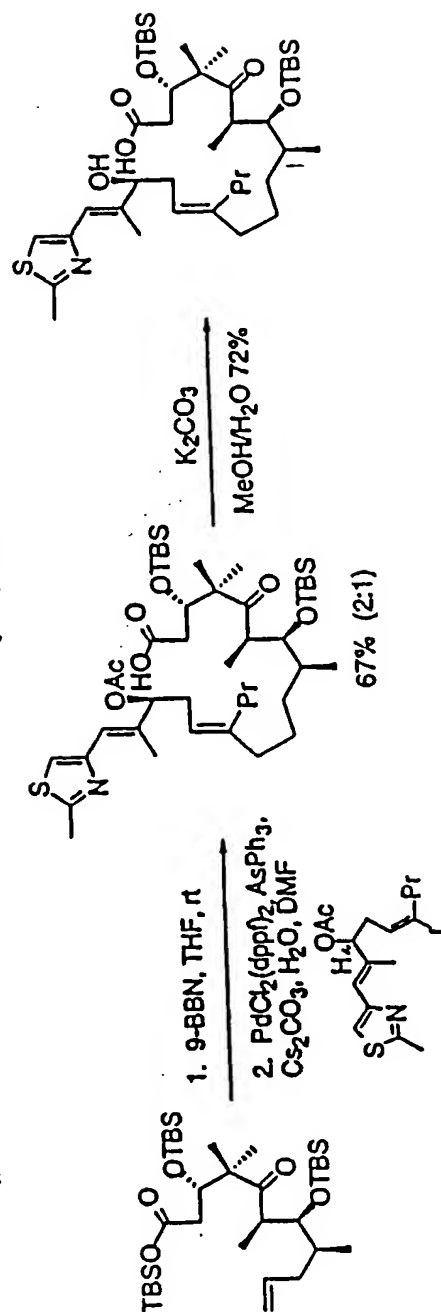


FIG. 23C

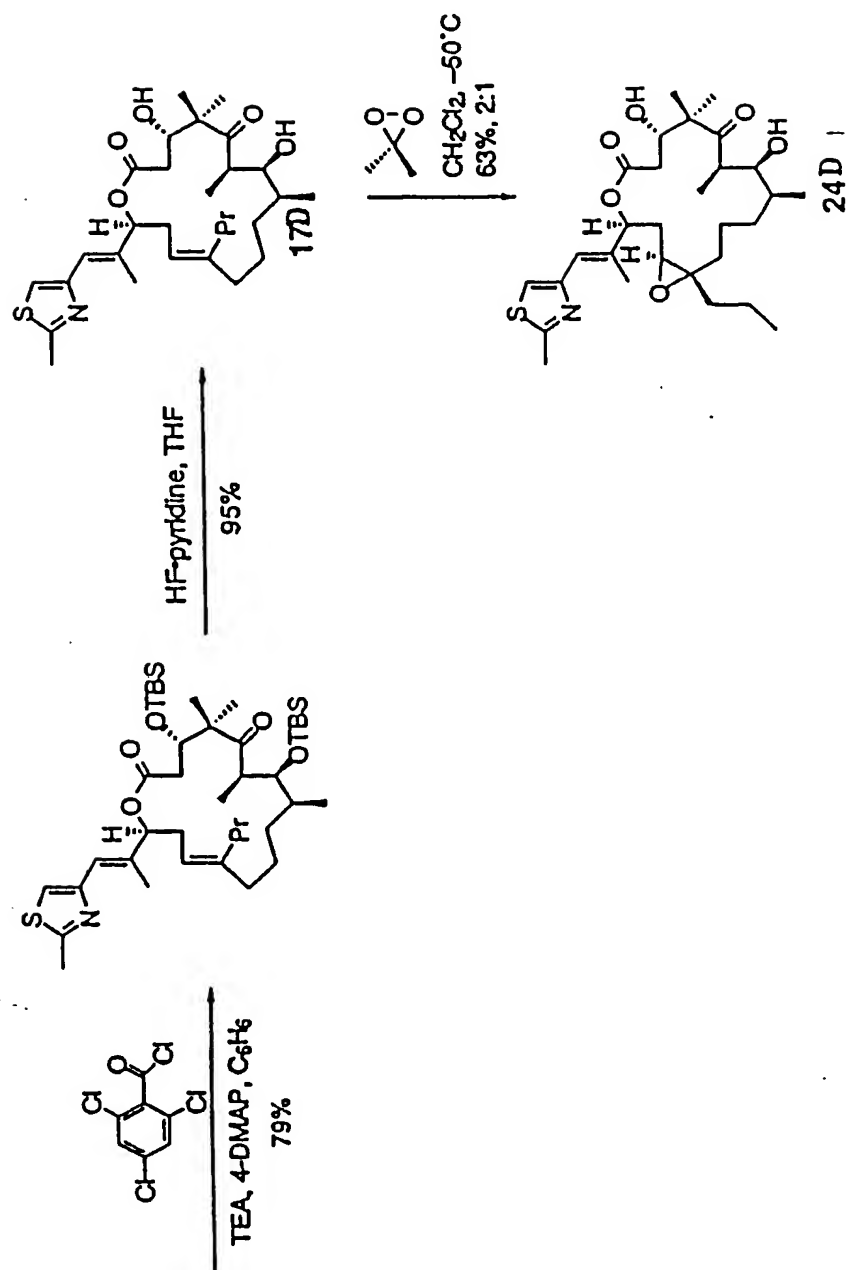


FIG. 24A

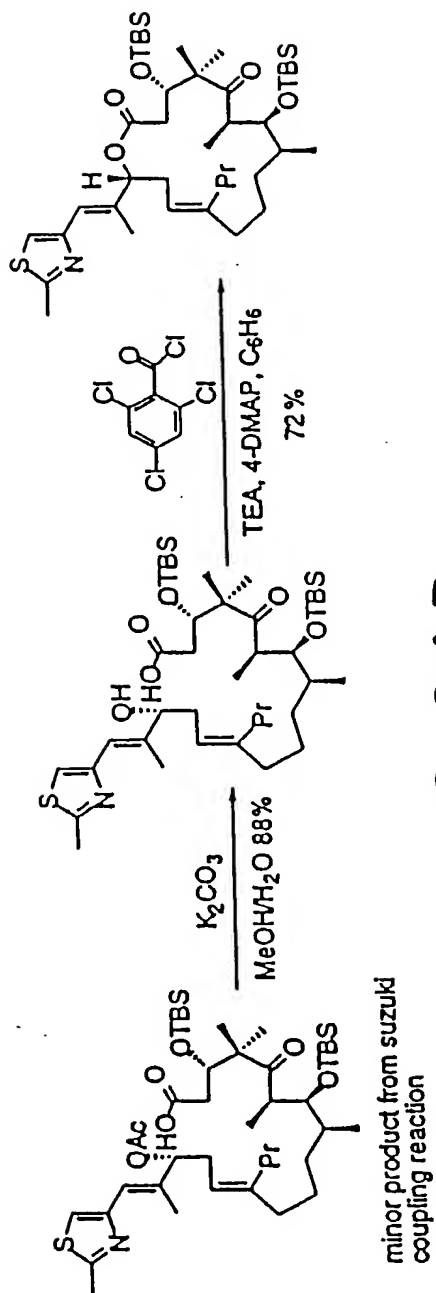


FIG. 24B

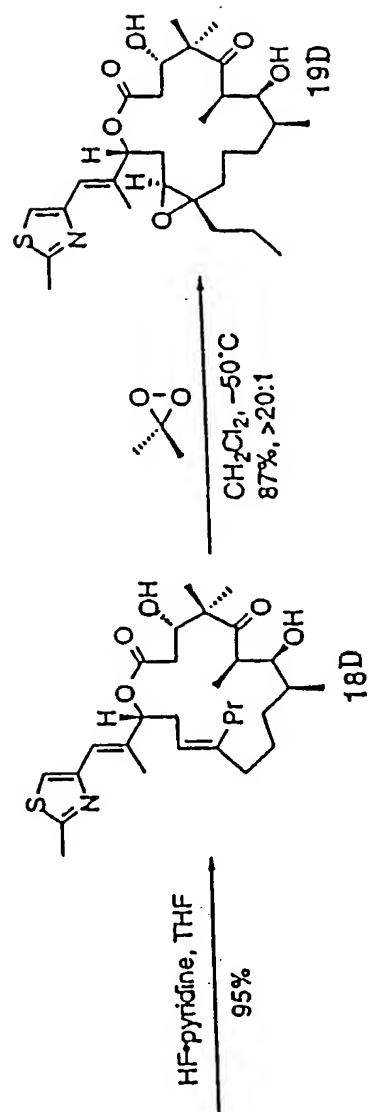


FIG. 25A

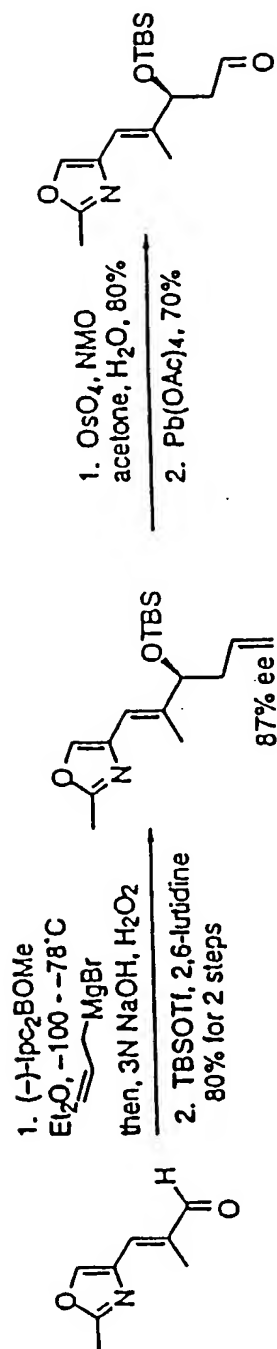


FIG. 25B

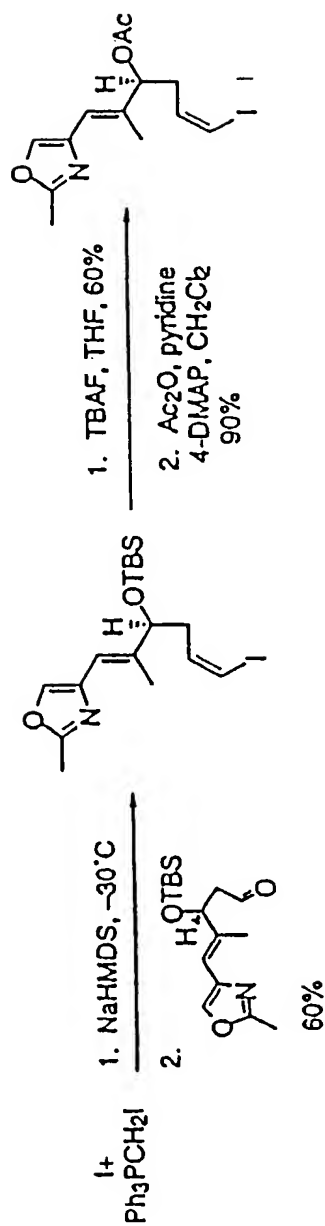


FIG. 25C

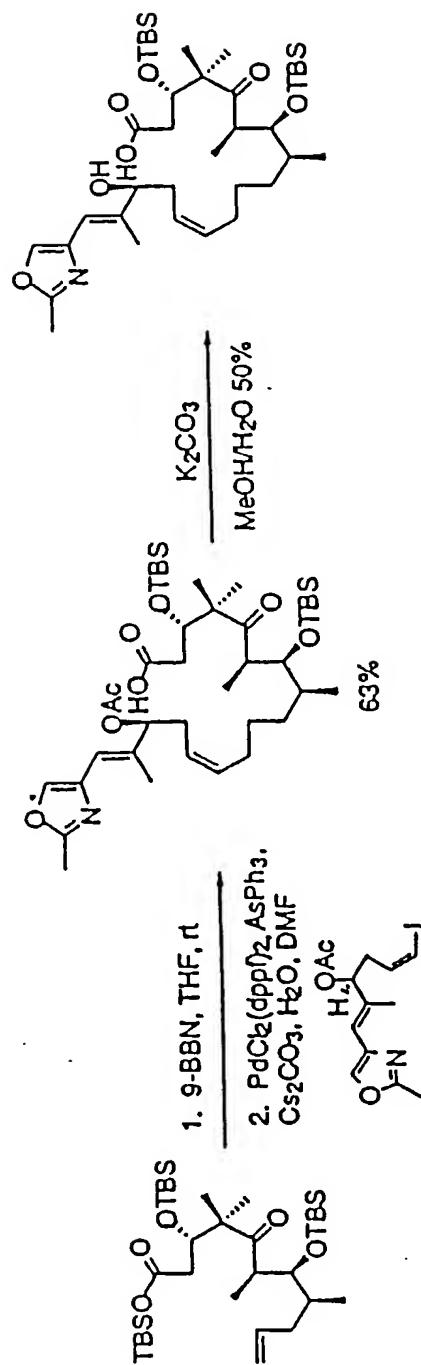


FIG. 25D

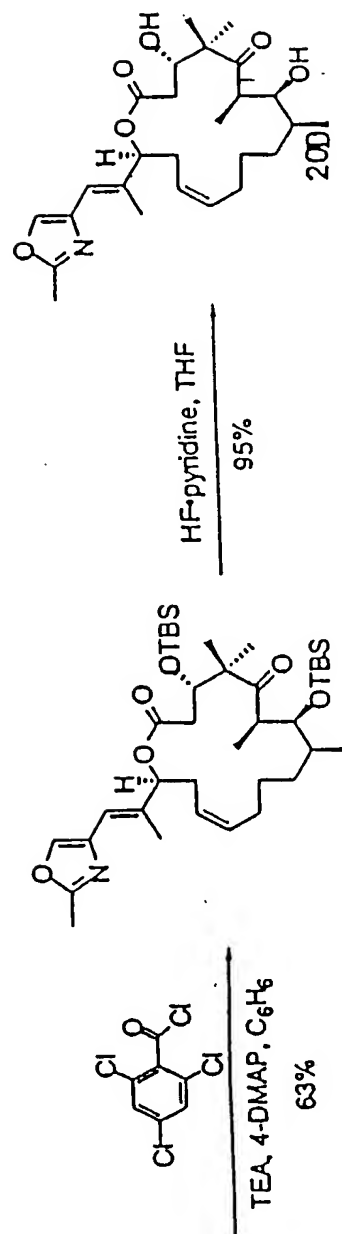


FIG. 26A

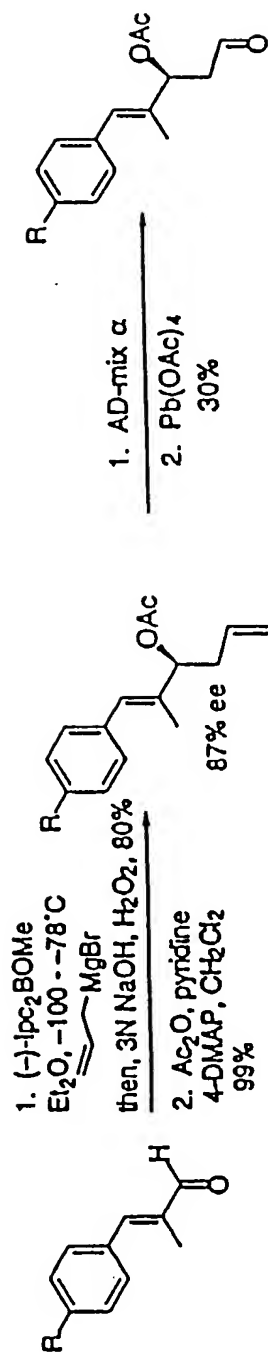
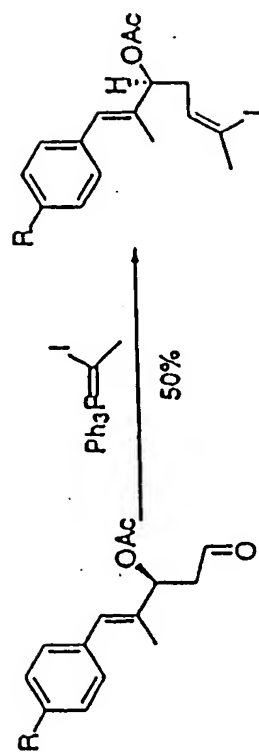


FIG. 26B



R = H, F, CF_3
 R=H is the only compound
 completed, F and CF_3 are nearly
 completed

FIG. 26C

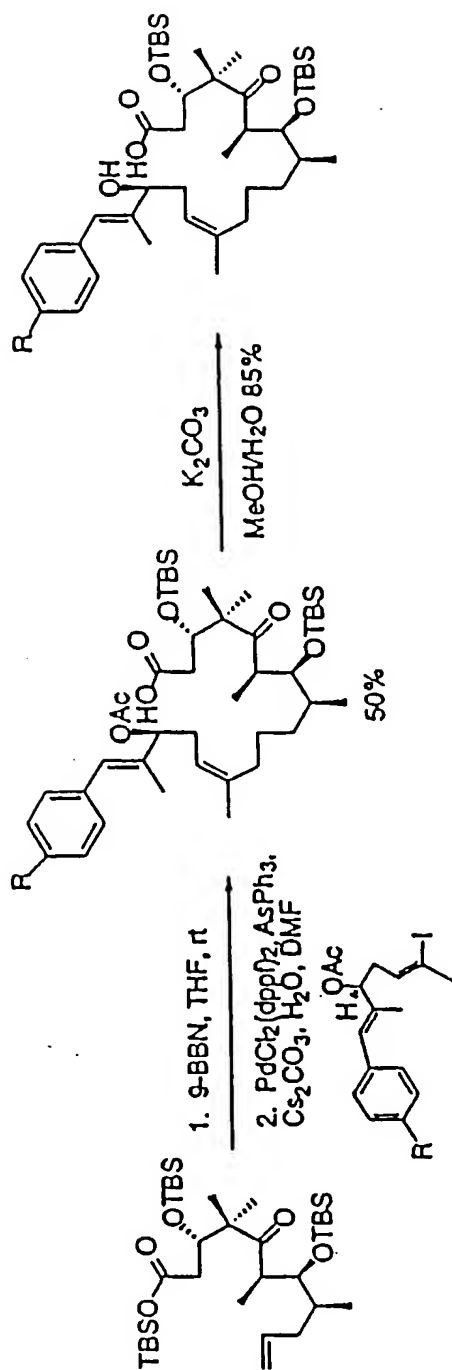


FIG. 26D

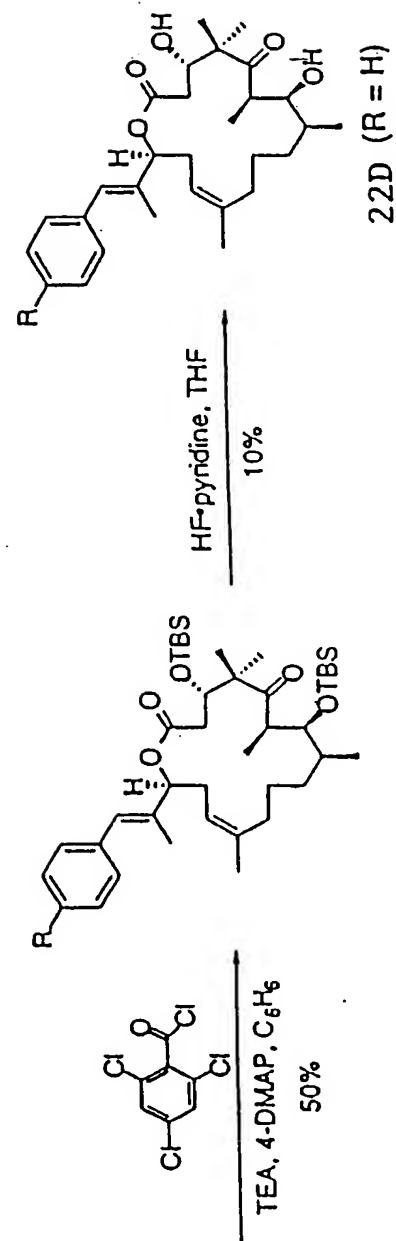


FIG. 27A

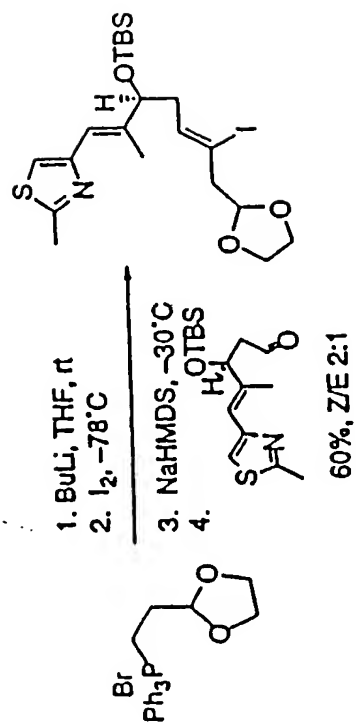


FIG. 27B

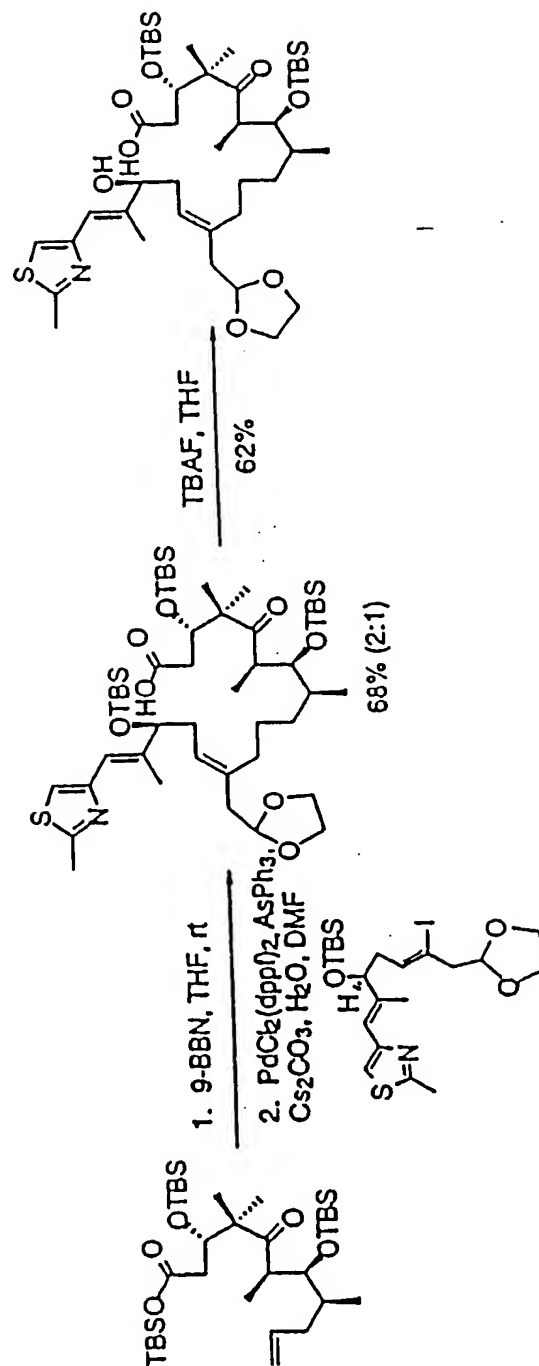
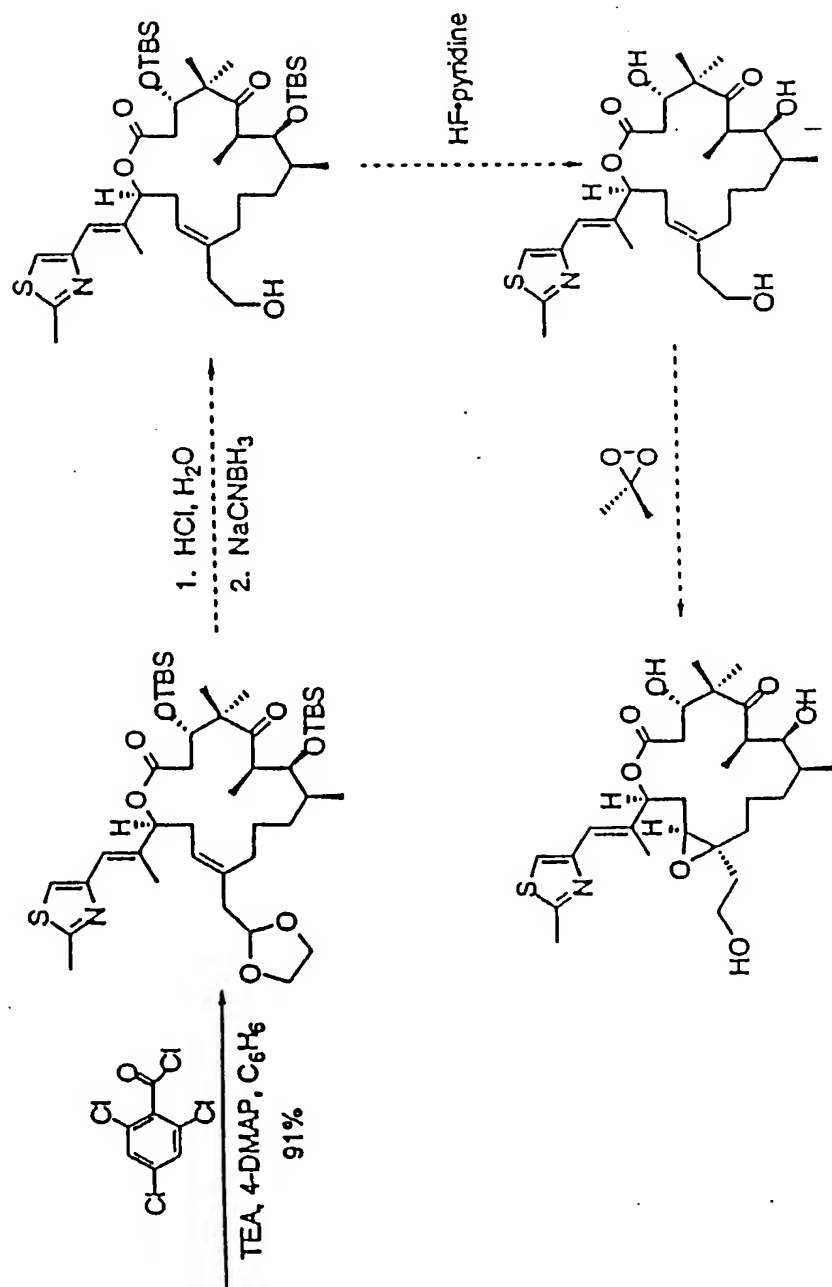
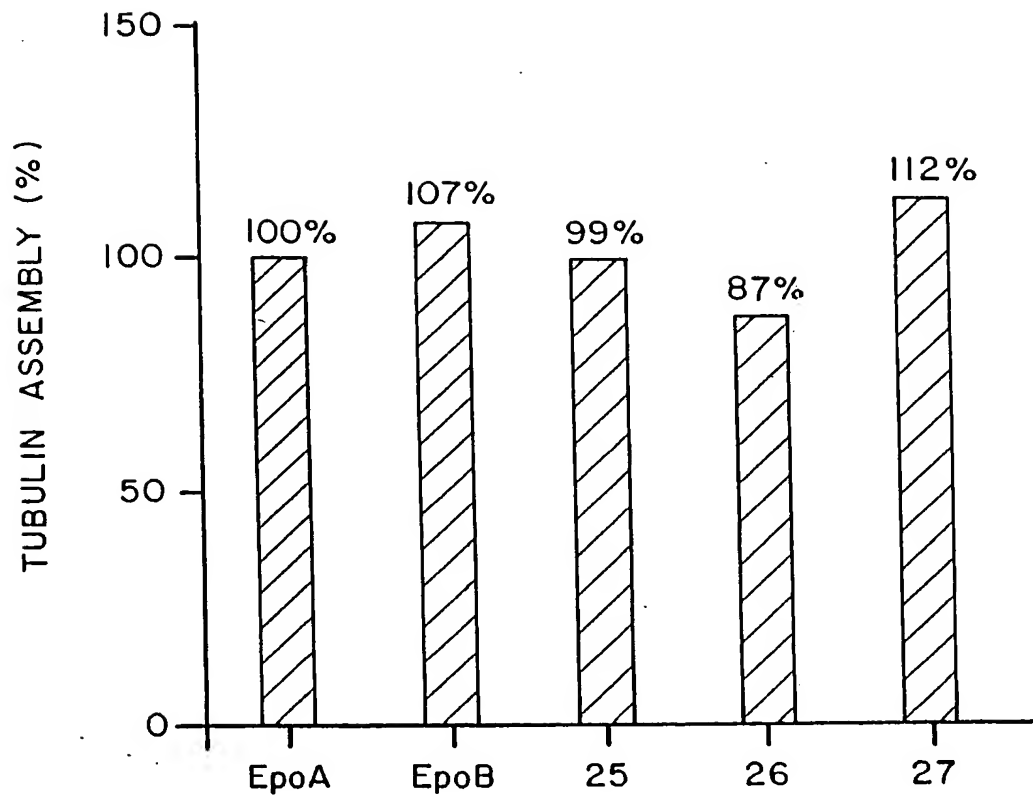


FIG. 27C



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FIG. 28A



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FIG. 28 B

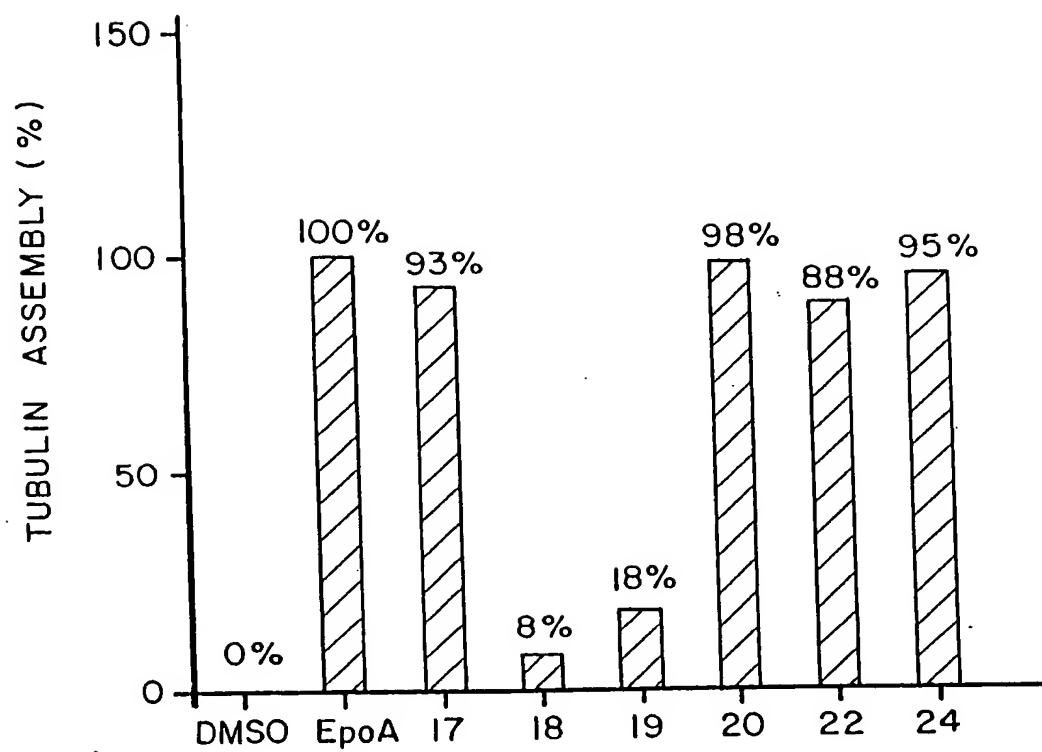


FIG. 29

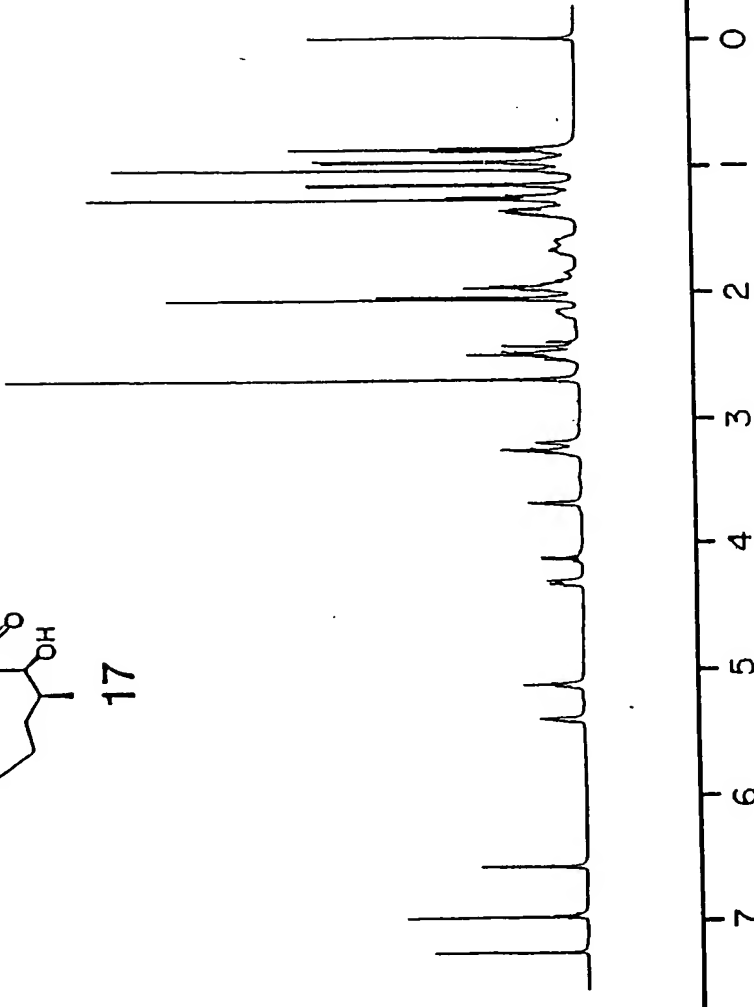
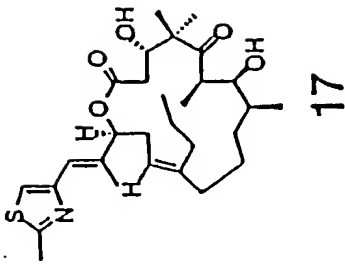


FIG. 30

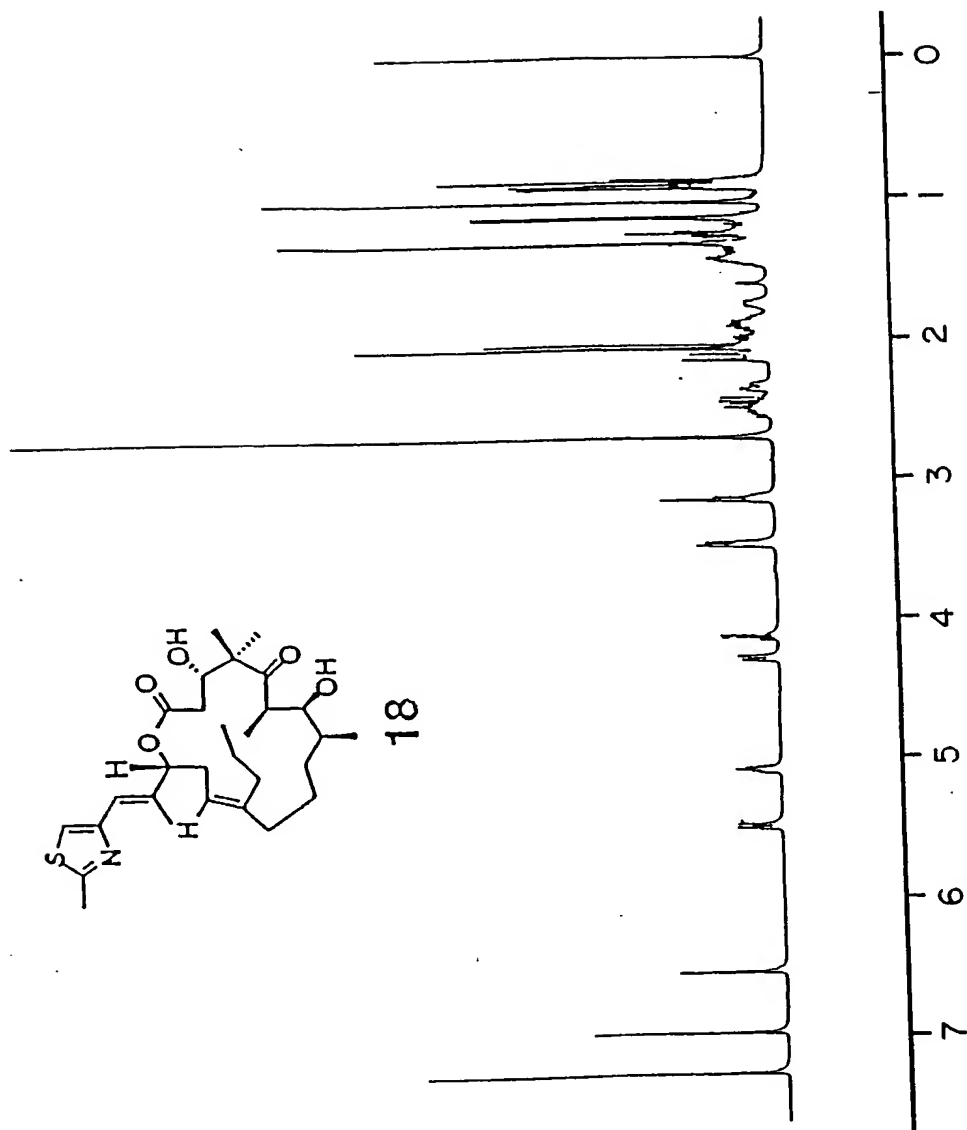
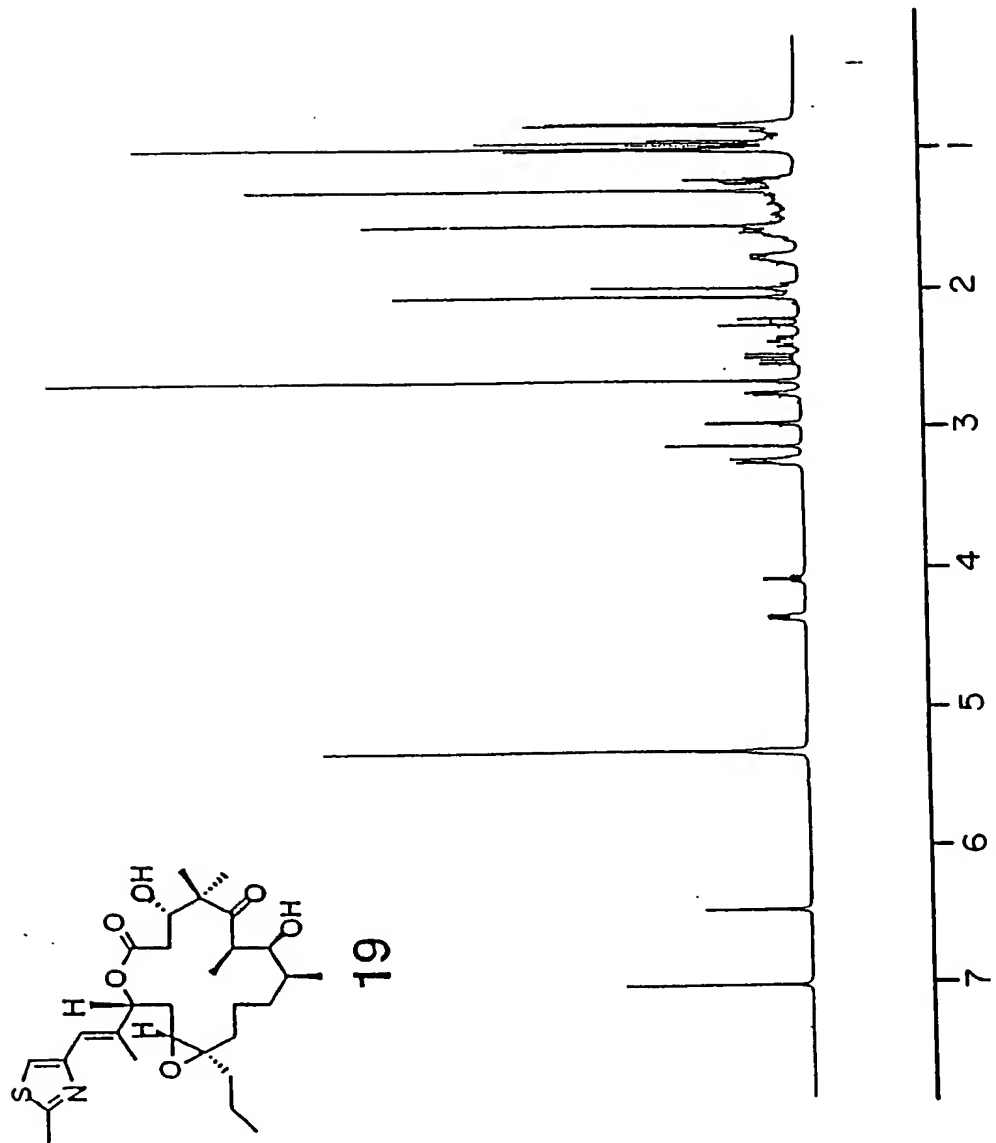
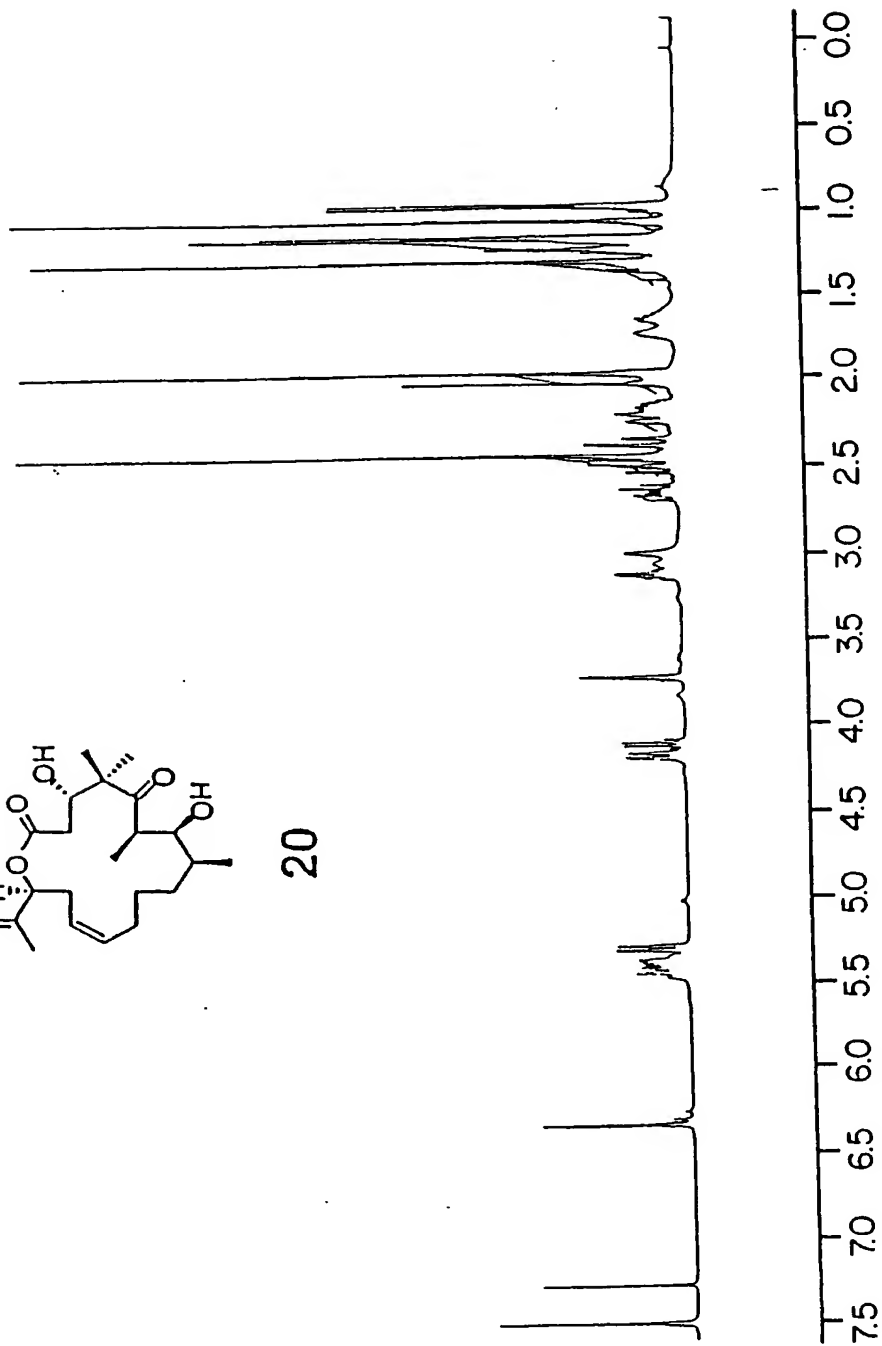
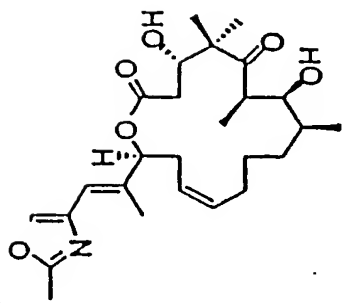


FIG. 31

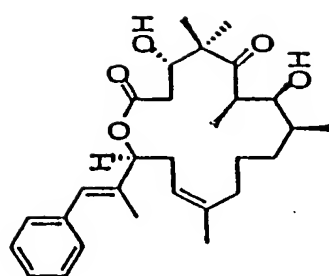


20



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FIG. 33



22

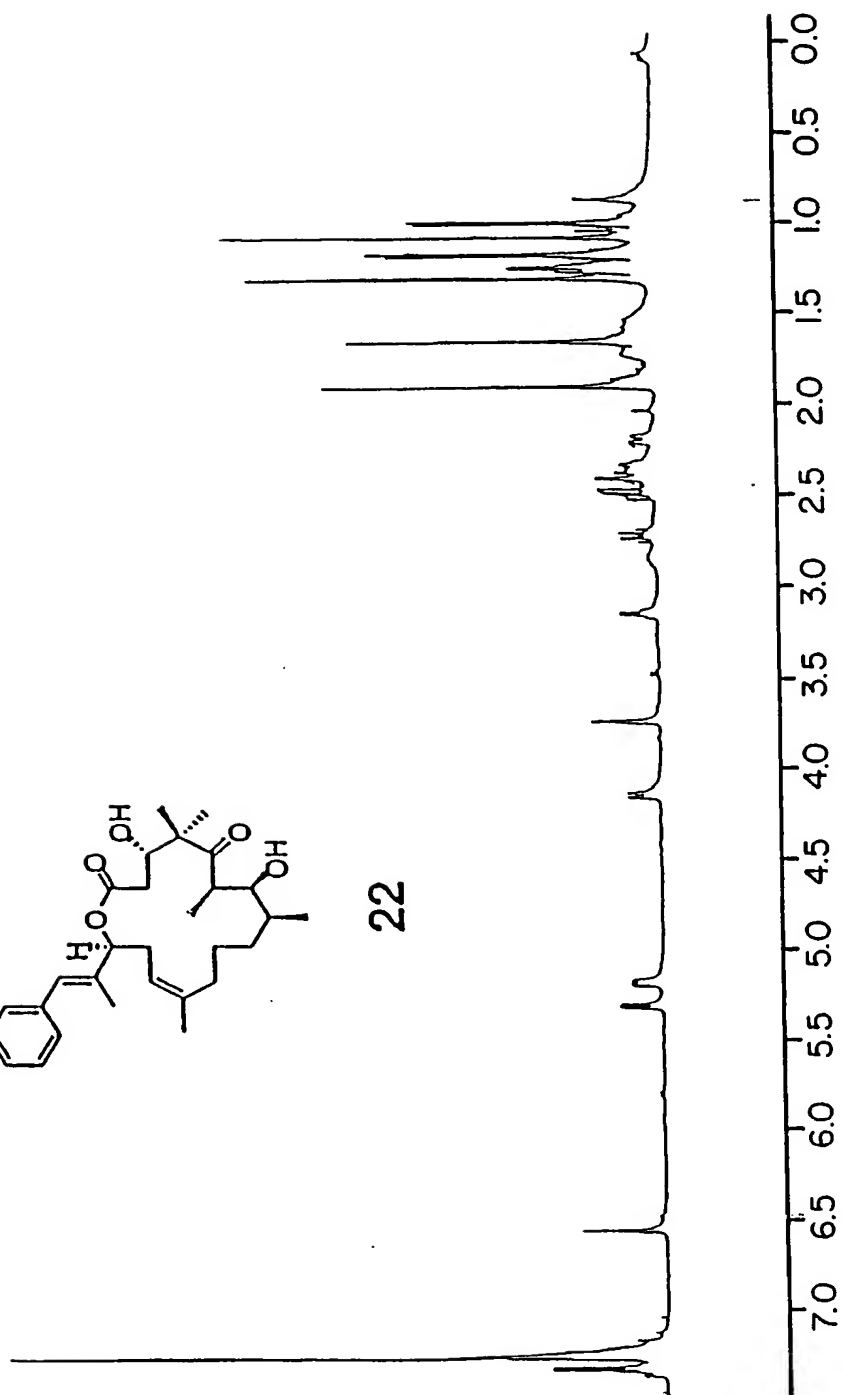
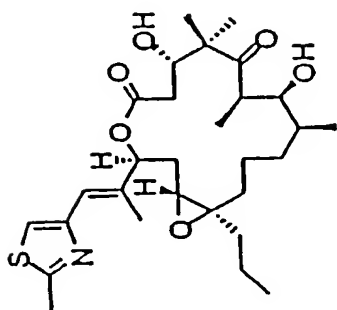
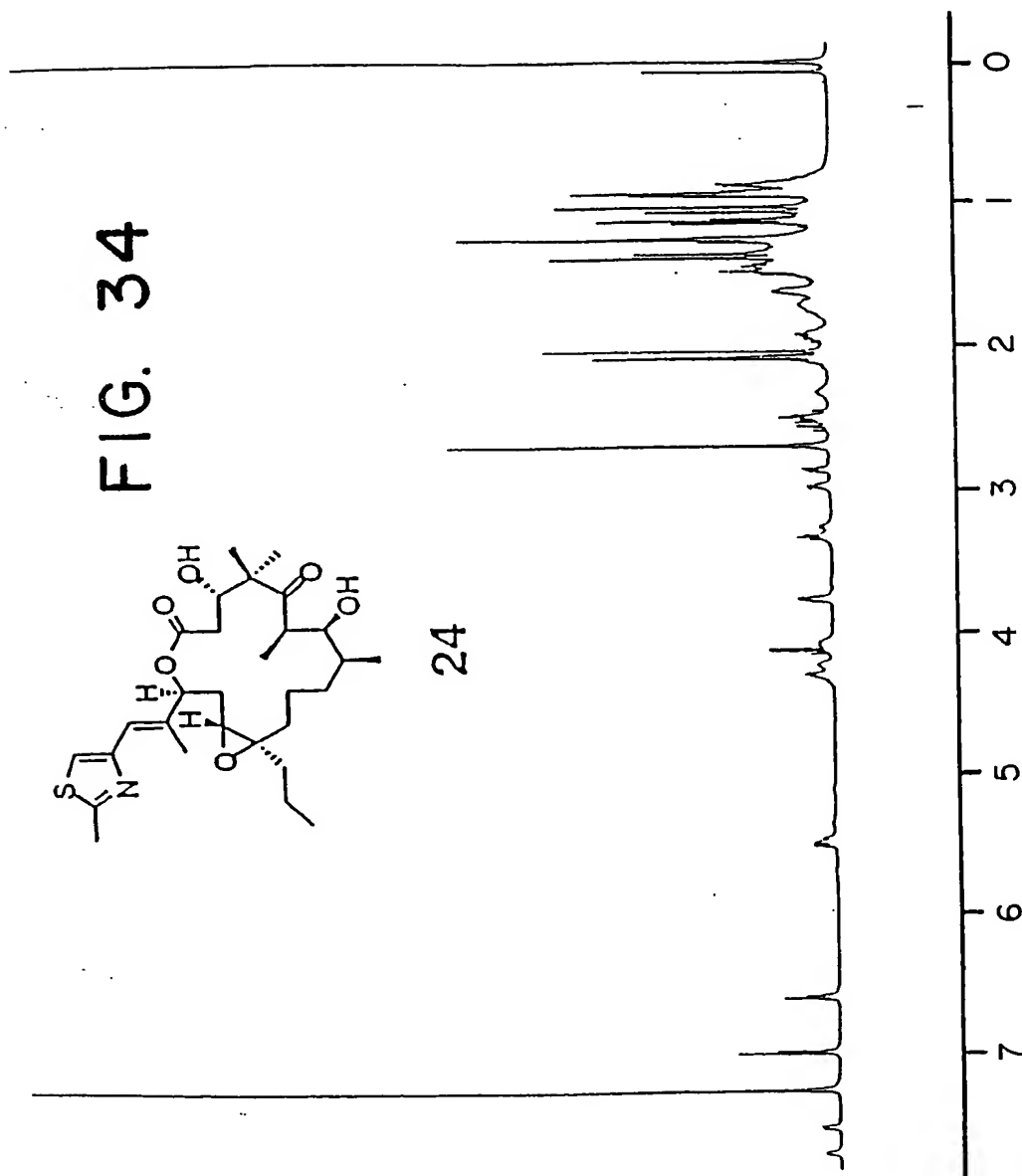


FIG. 34

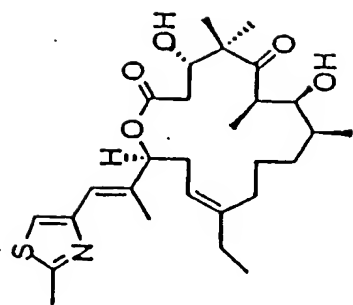


24

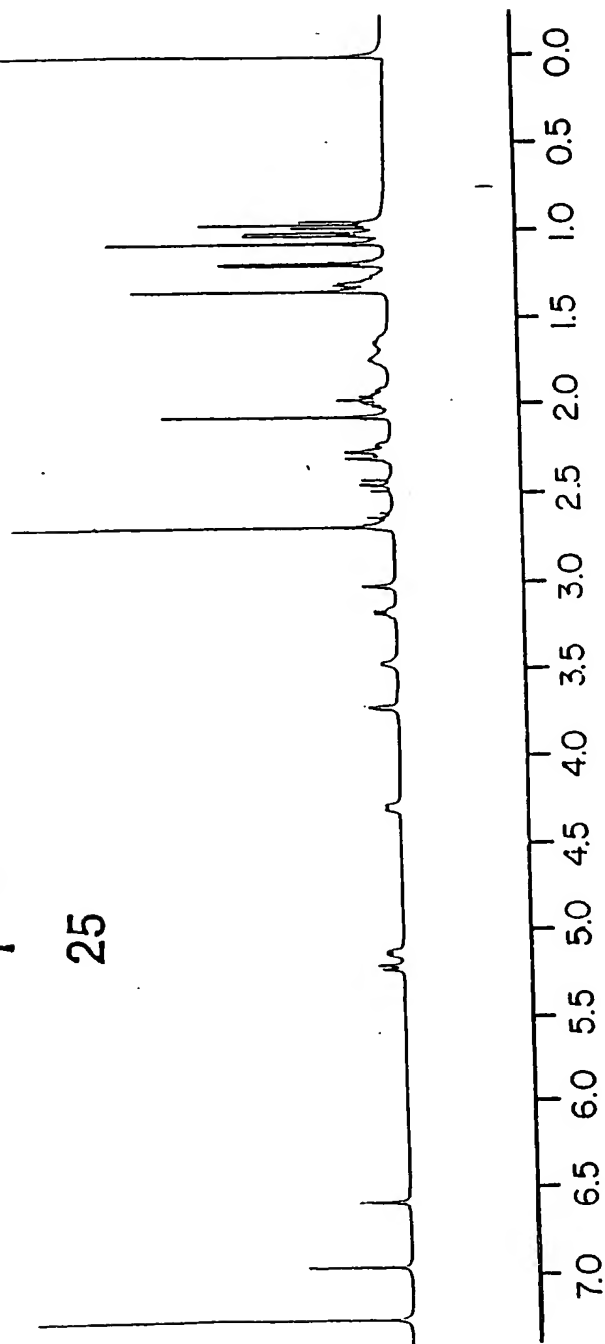


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FIG. 35

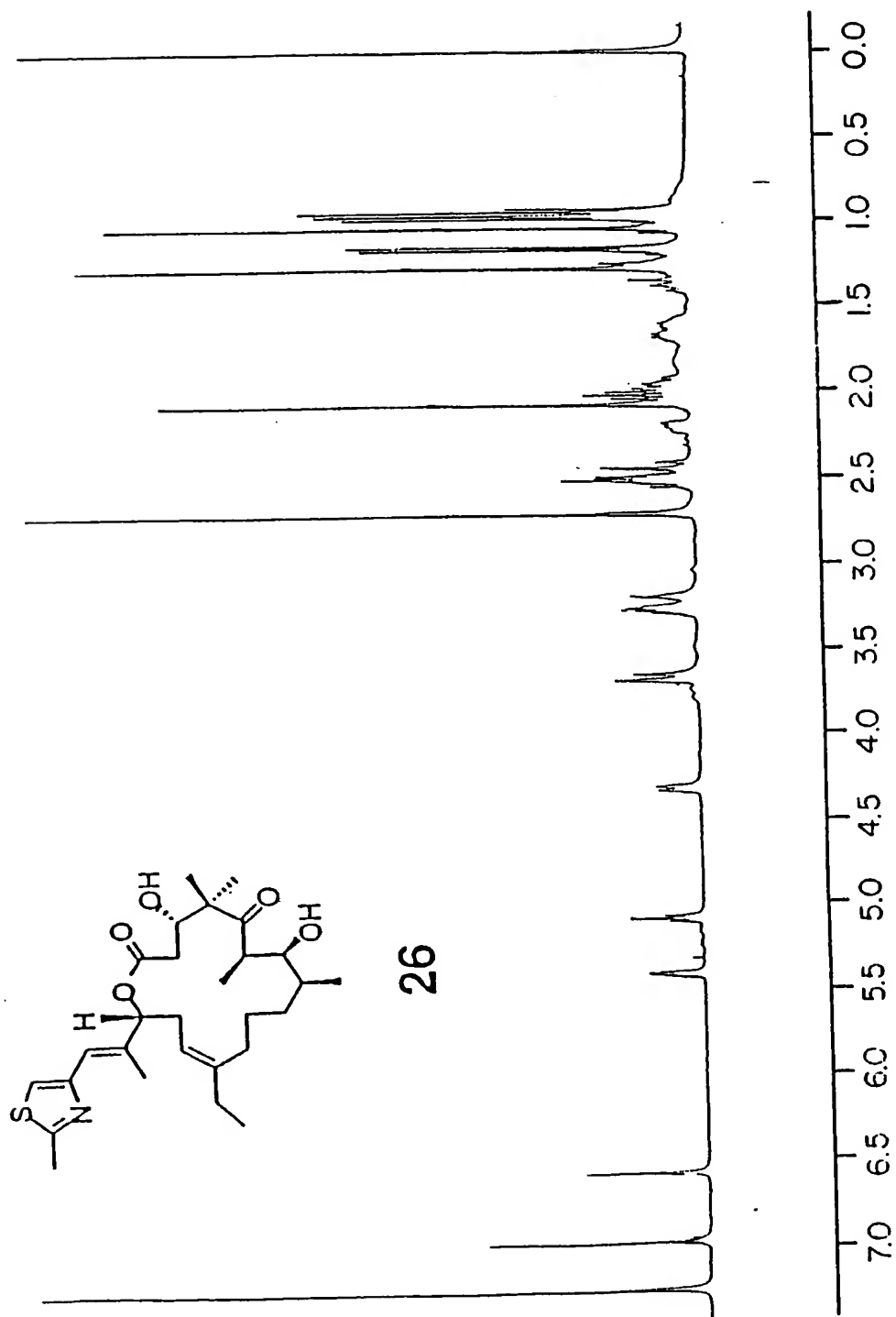


25



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FIG. 36



26

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FIG. 37

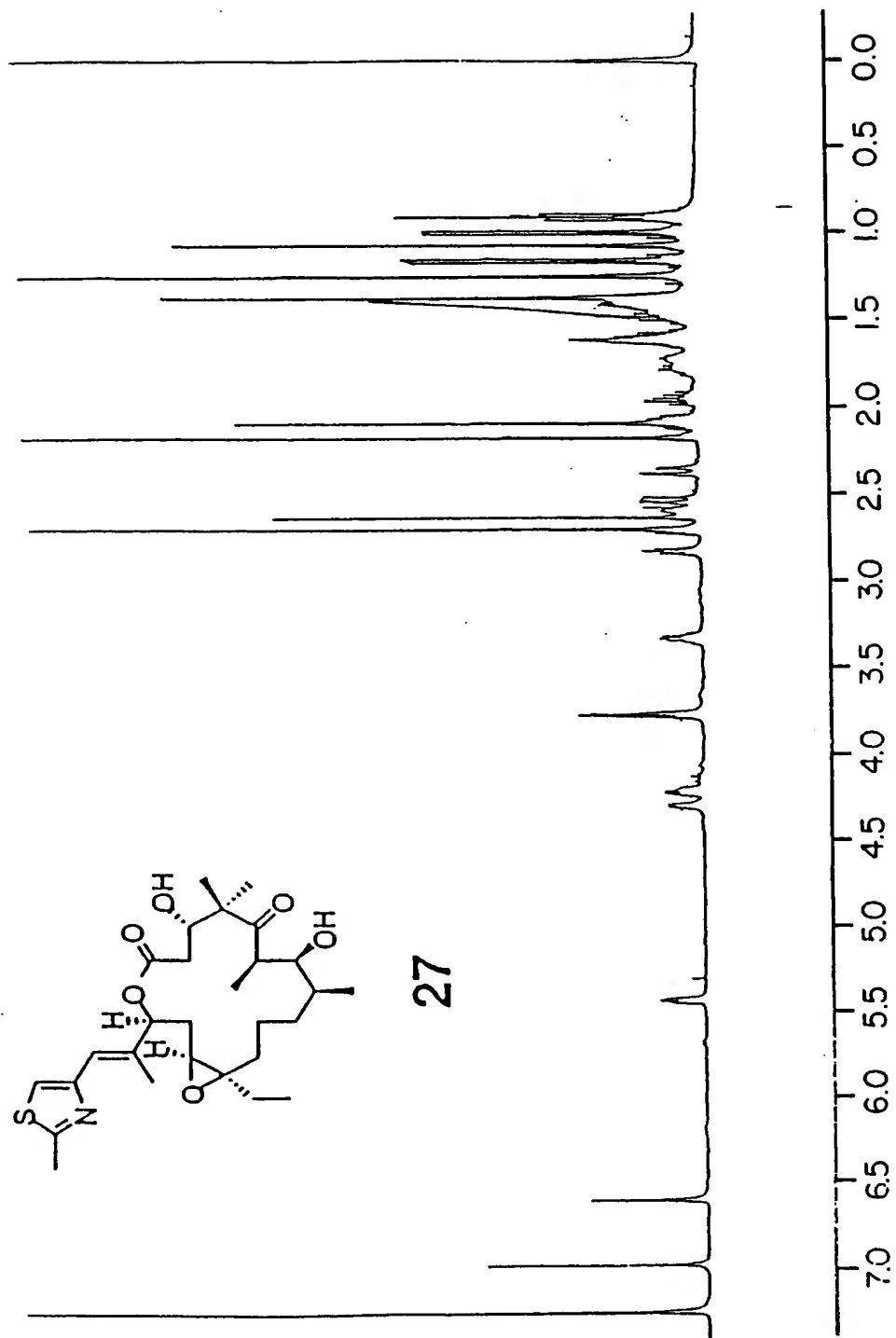
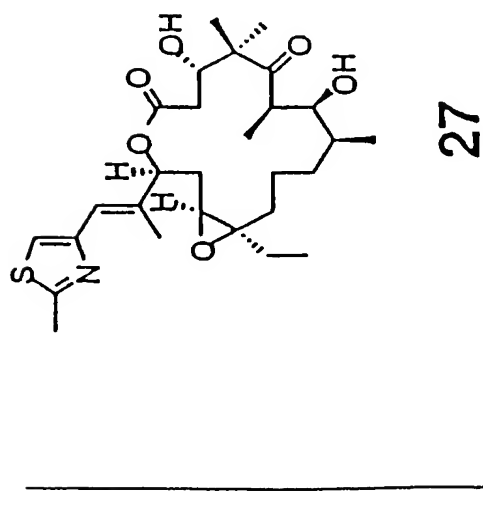
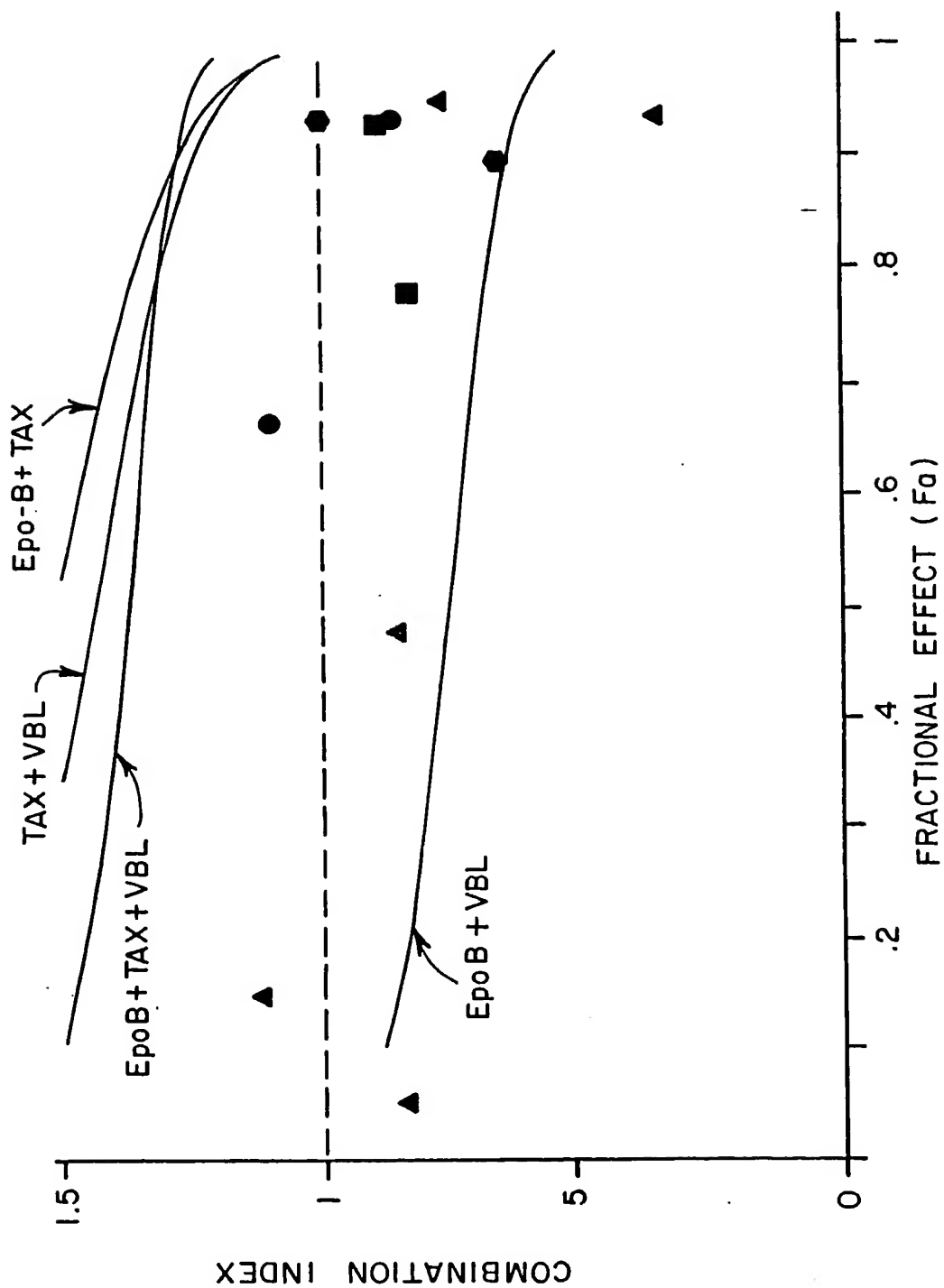
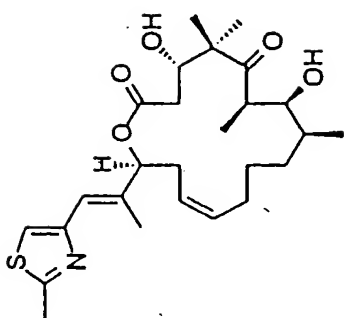


FIG. 38



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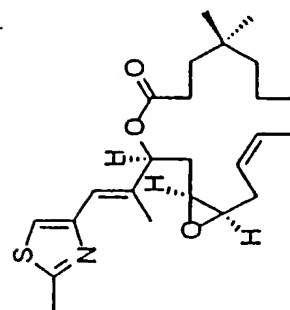
FIG. 39A



desoxyepothilone A

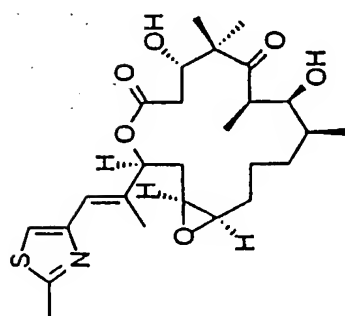
1

(0.022)
[0.012]



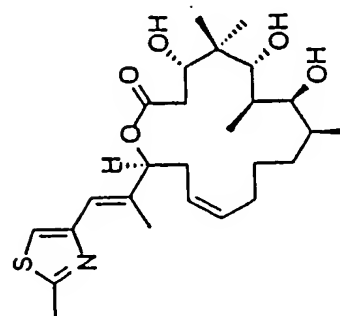
3

(271.1)
[22.4]



epothilone A

(0.0027)
[0.020]



2

(14.23)
[6.28]

4

(2.12)
[43.0]

FIG. 39B

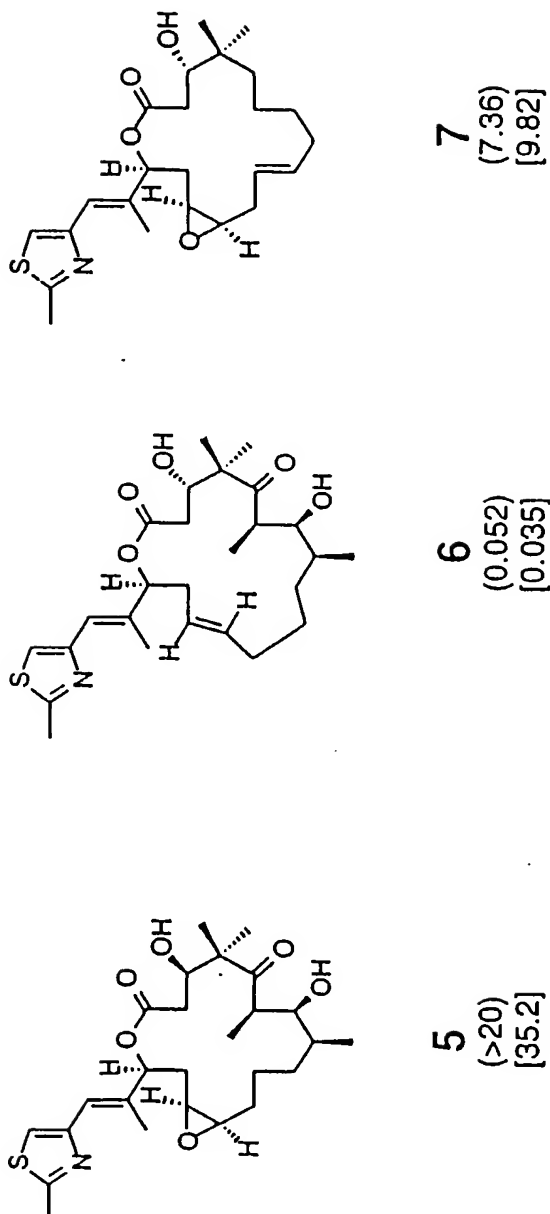
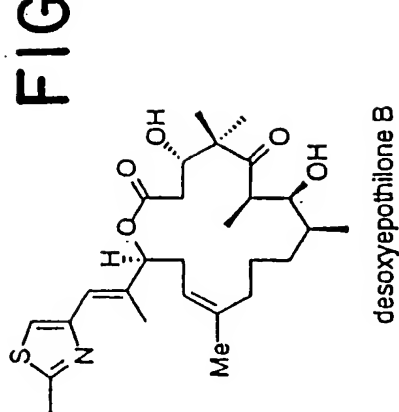
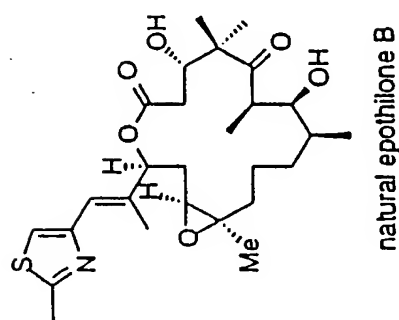


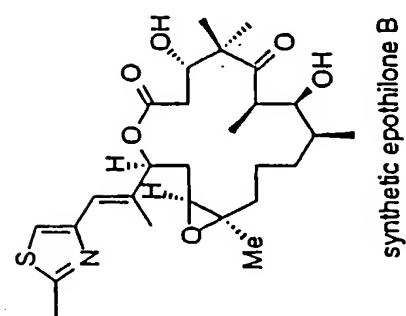
FIG. 40A



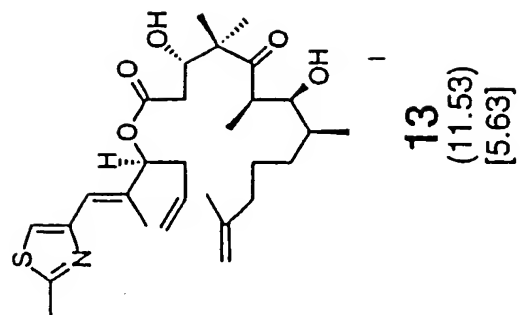
10
(0.0095)
[0.017]



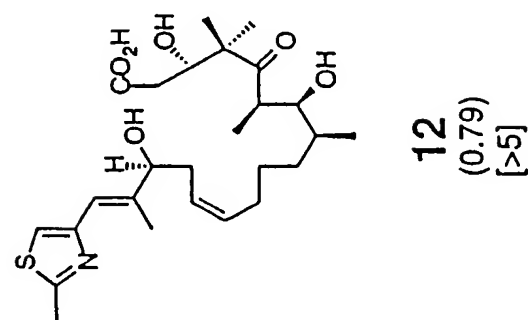
9
(0.00017)
[0.0012]



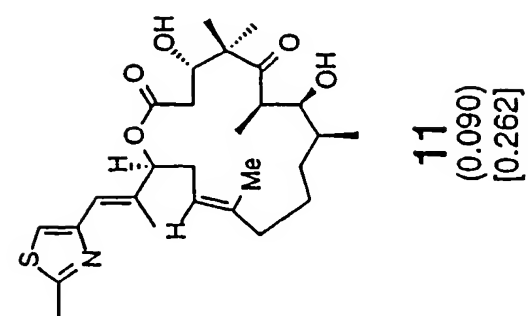
8
(0.00044)
[0.0026]



13
(11.53)
[5.63]



12
(0.79)
[>5]



11
(0.090)
[0.262]

FIG. 40B

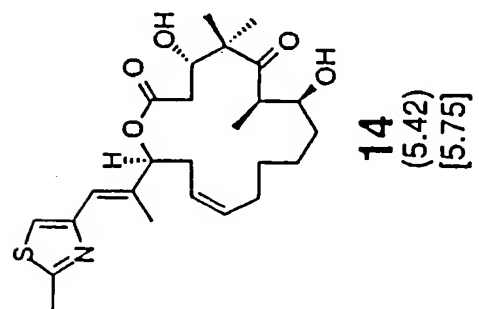
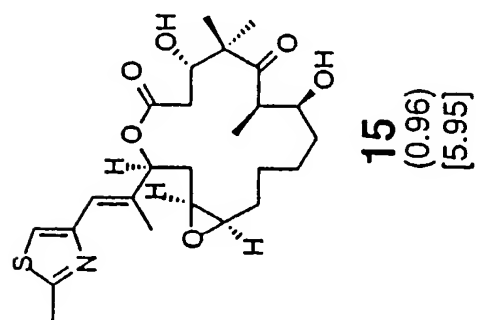
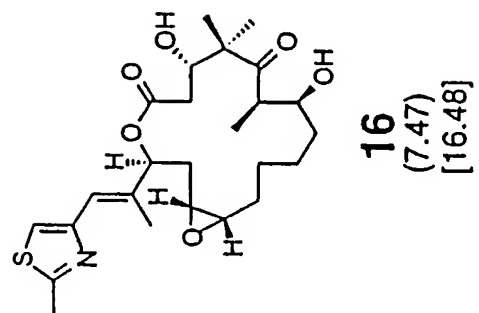
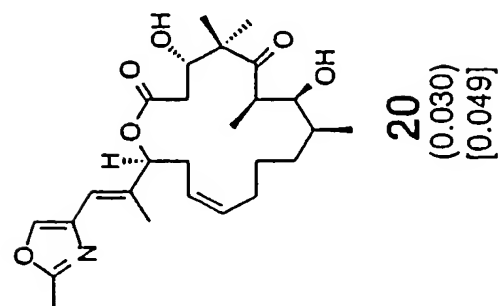
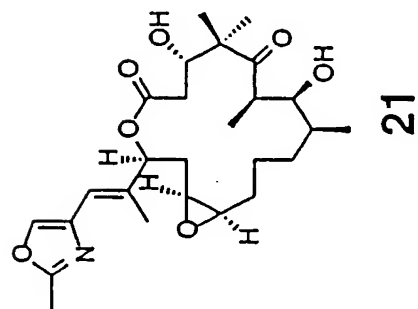
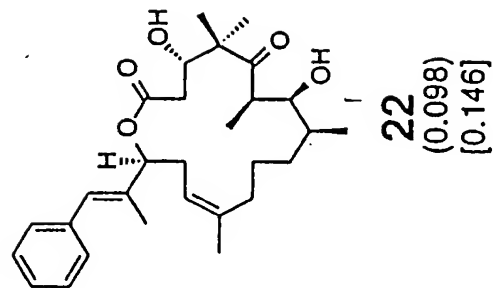
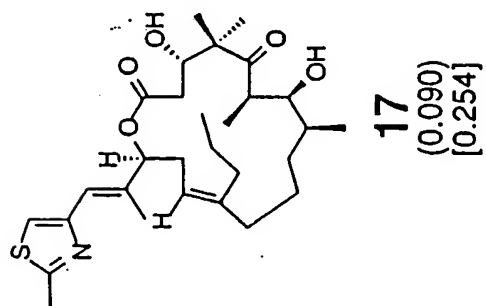
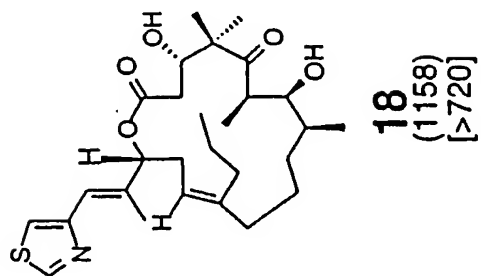
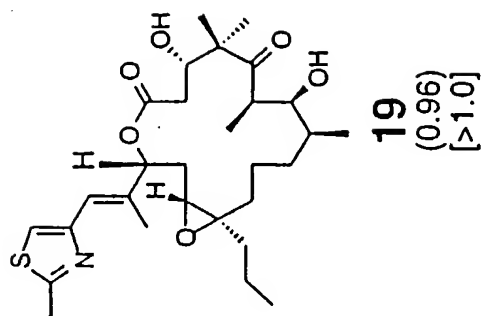


FIG. 41A



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FIG. 41B

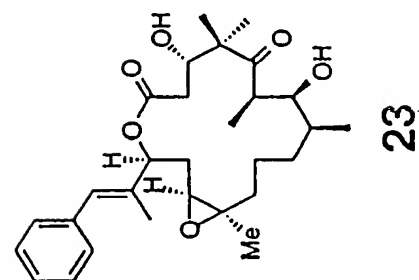
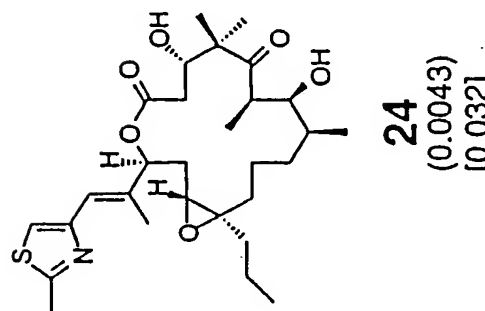
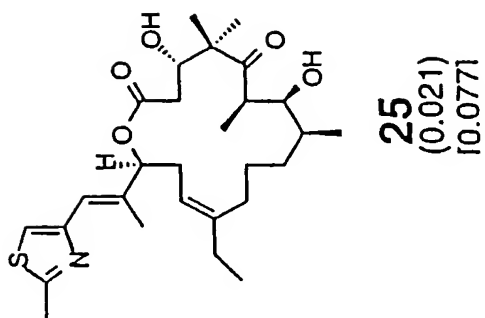


FIG. 42A

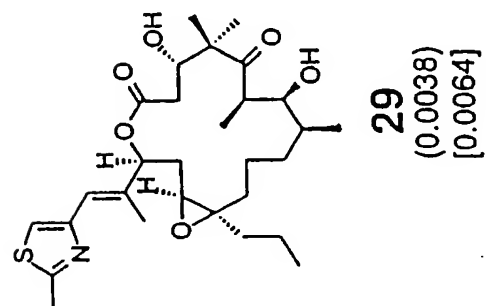
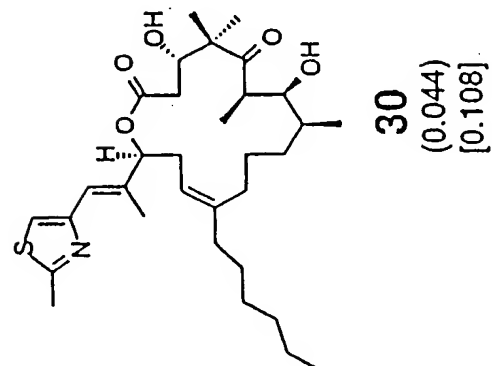
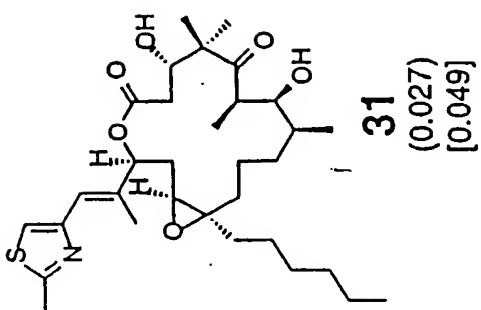
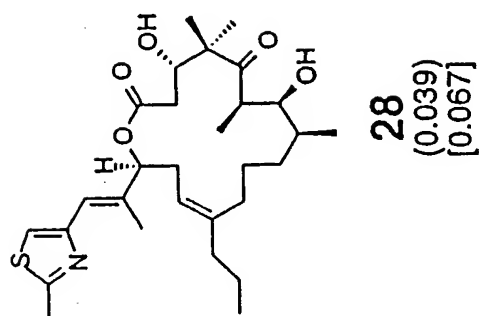
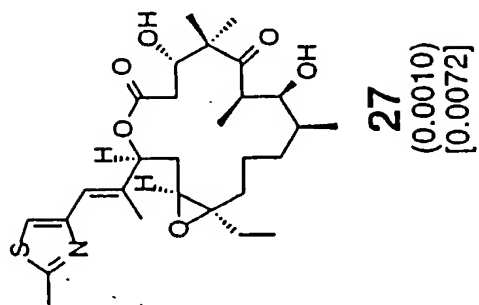
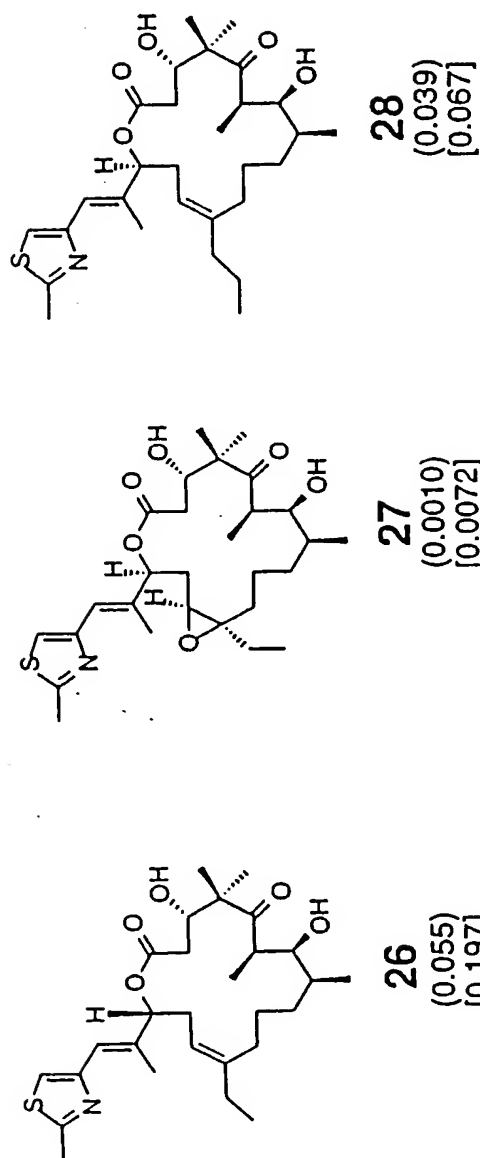


FIG. 42B

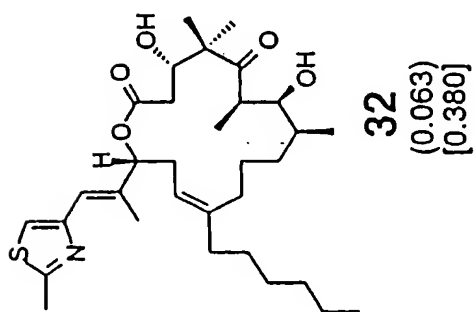
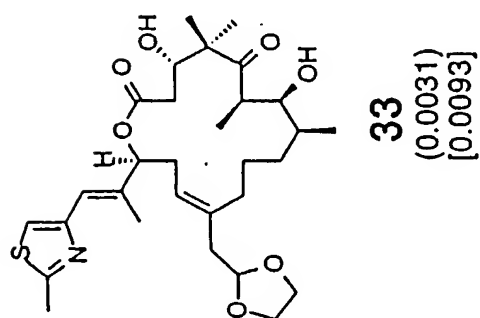
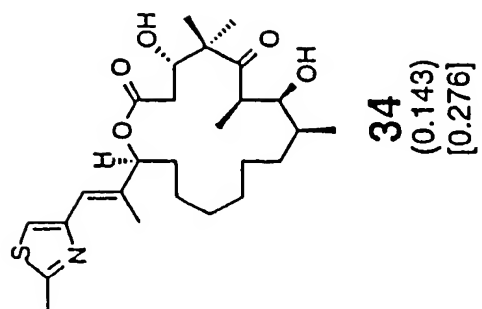


FIG. 42C

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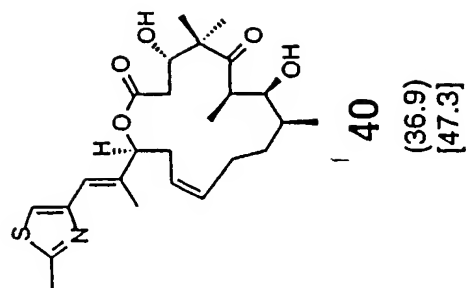
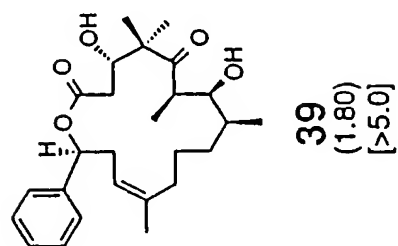
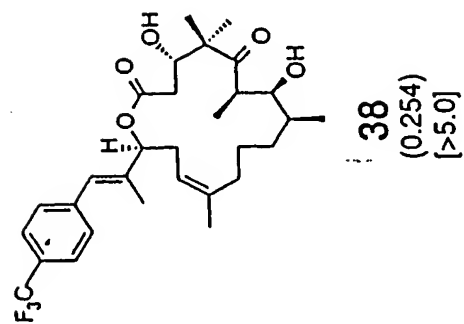
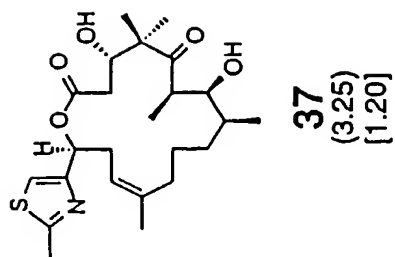
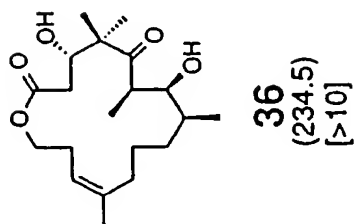
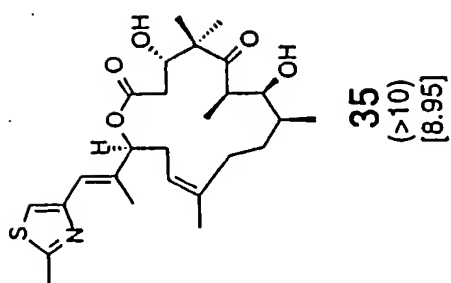


FIG. 42D

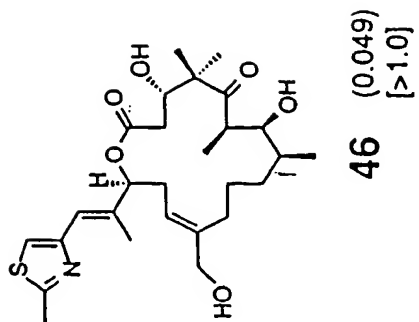
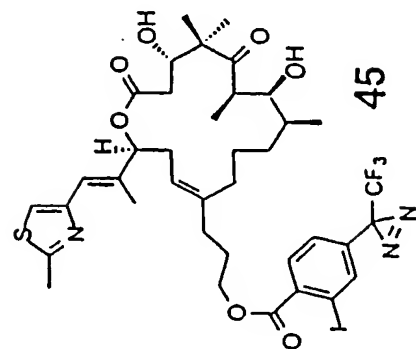
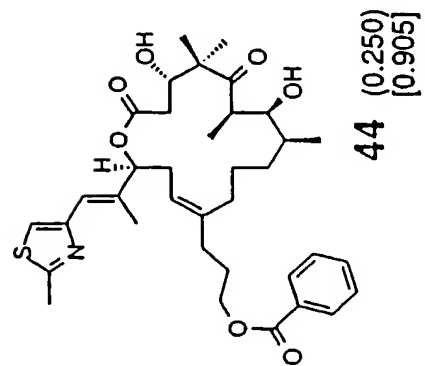
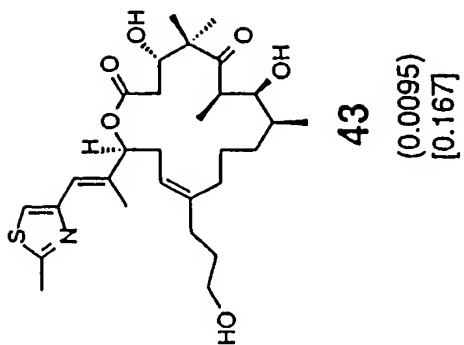
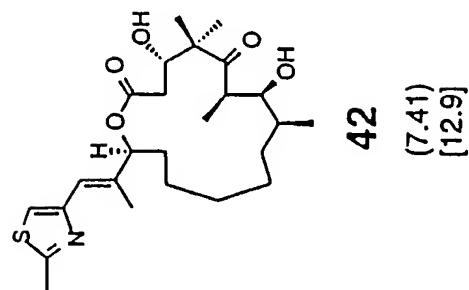
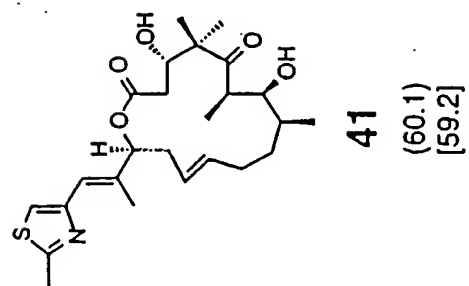
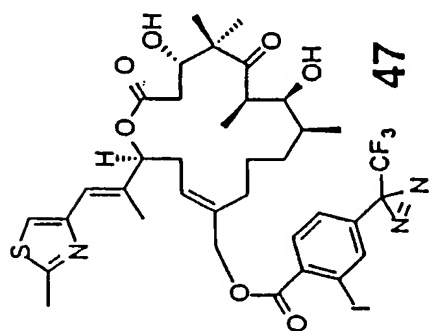
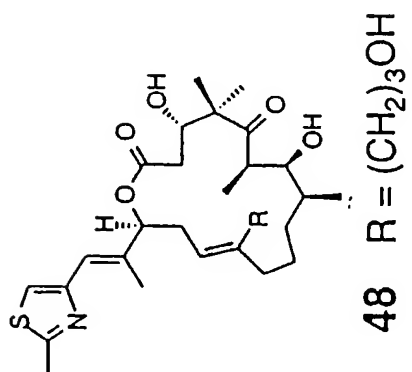
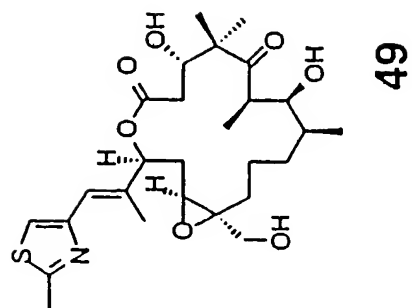
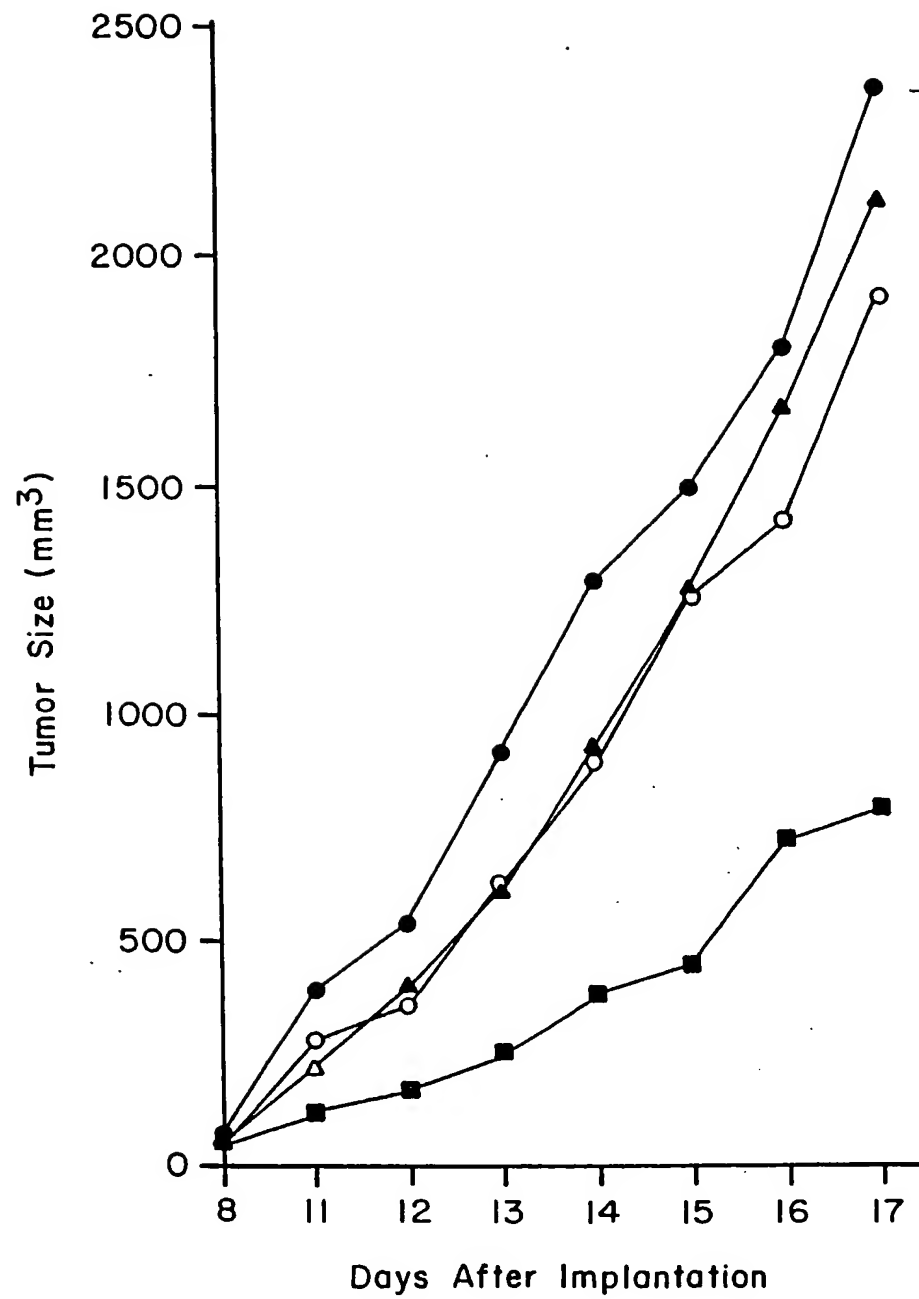


FIG. 42E



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FIG. 43 A



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FIG. 43 B

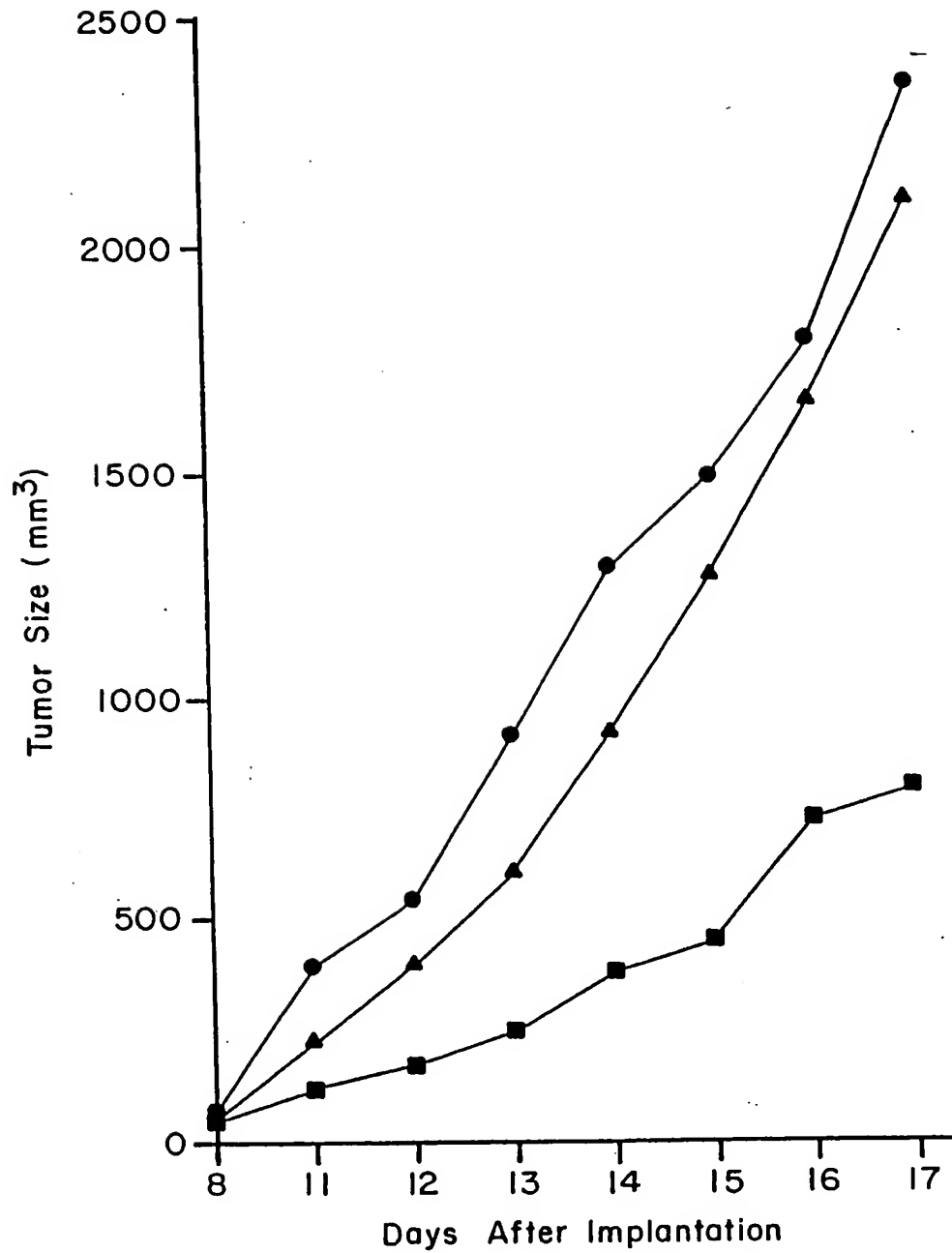


FIG. 44A

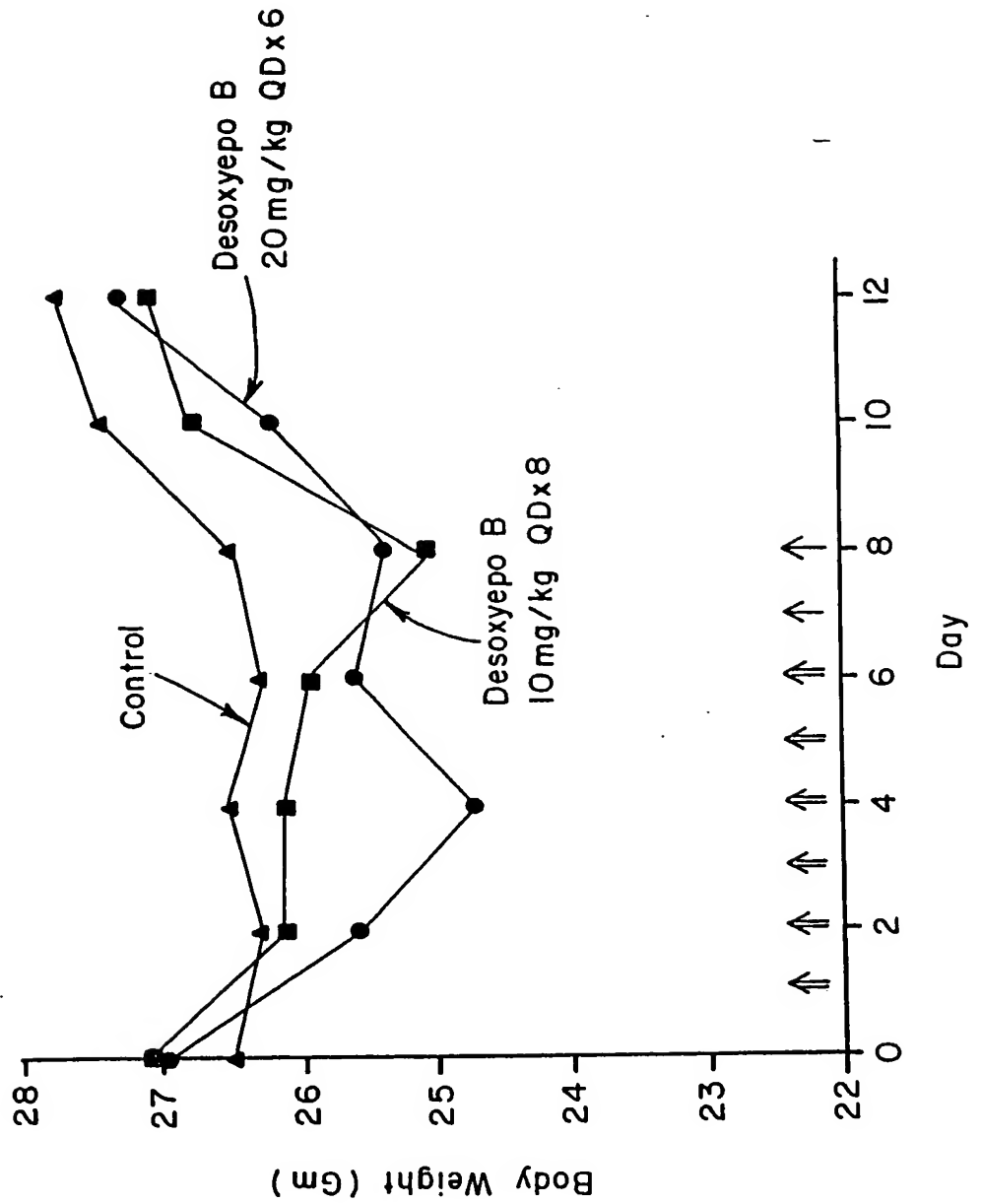
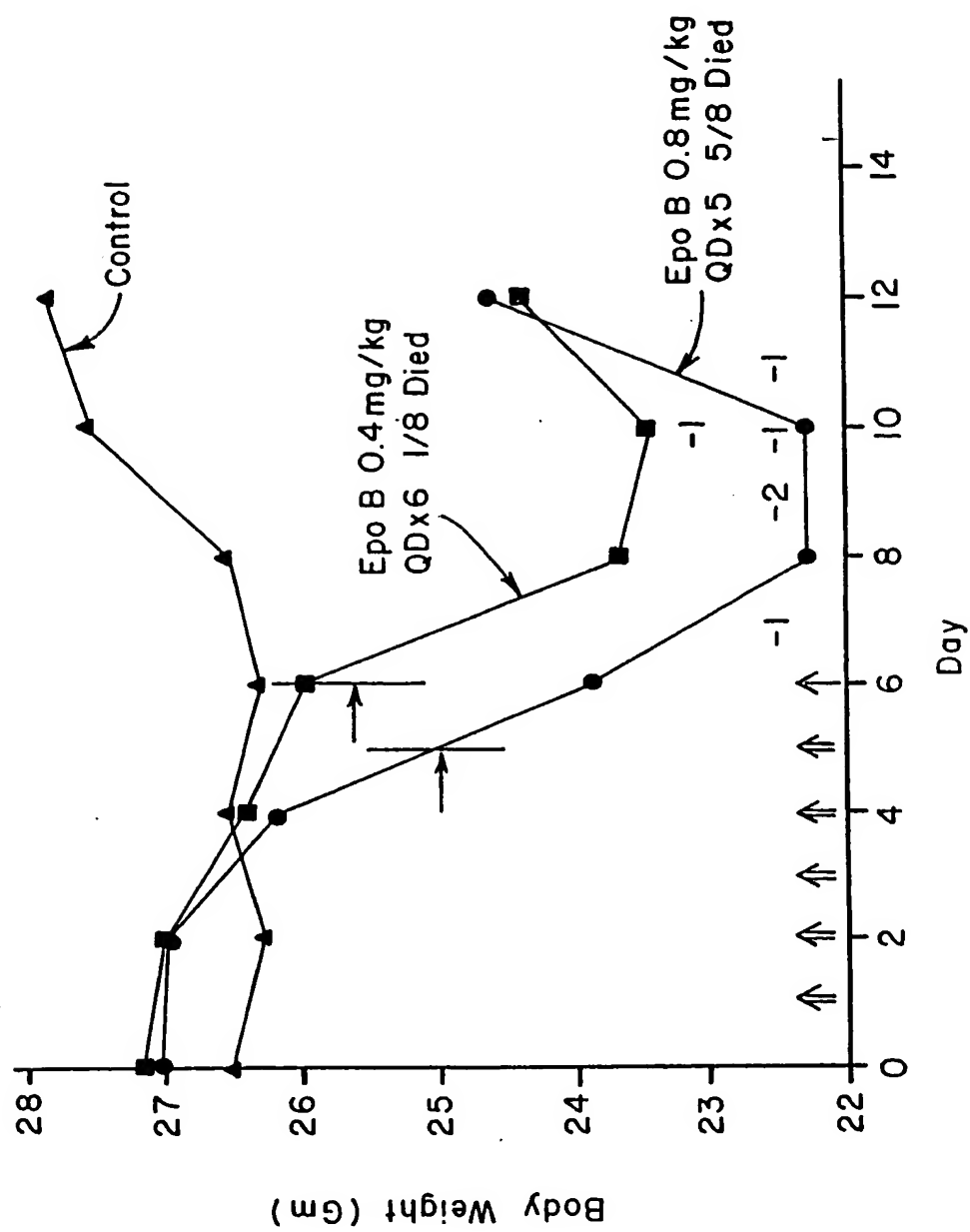
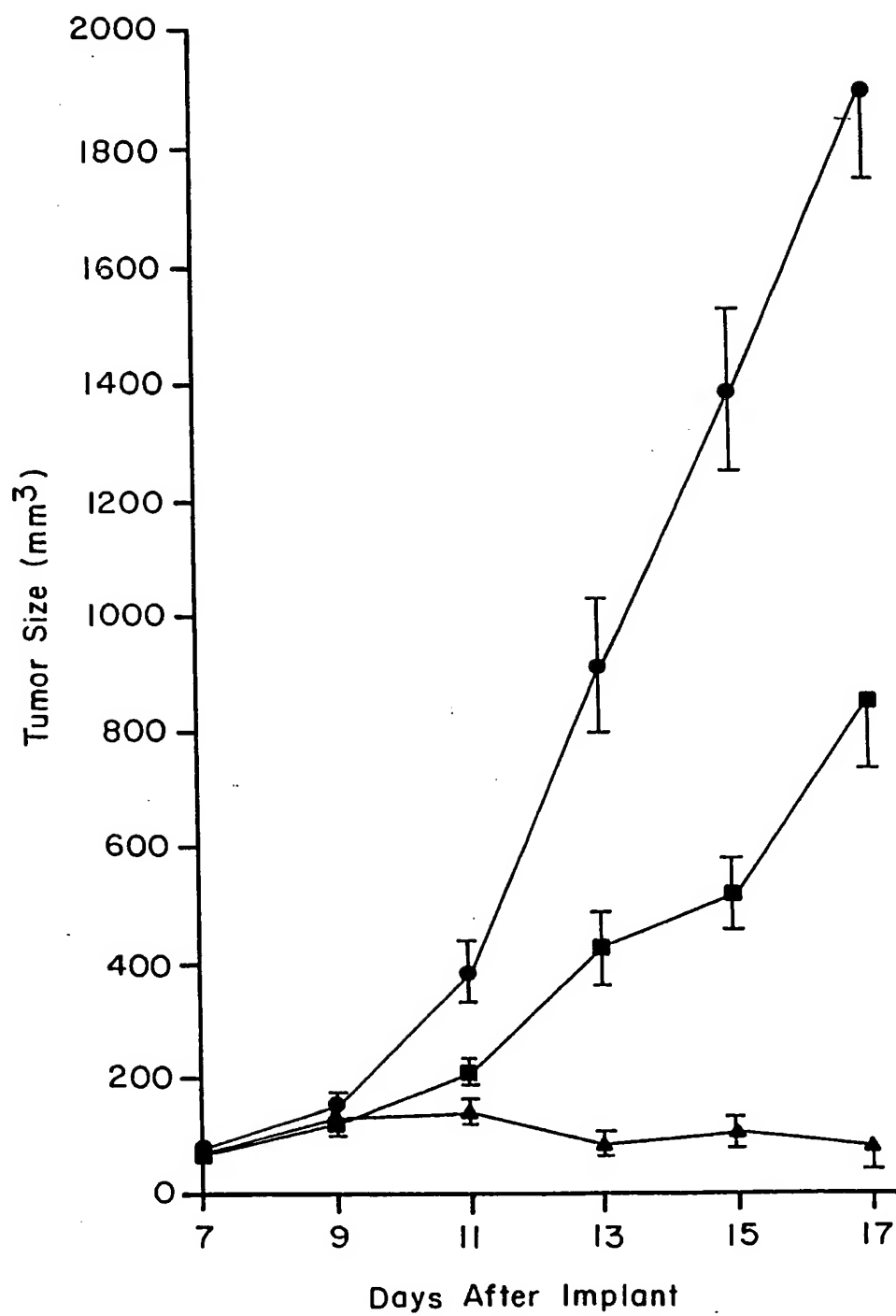


FIG. 44B



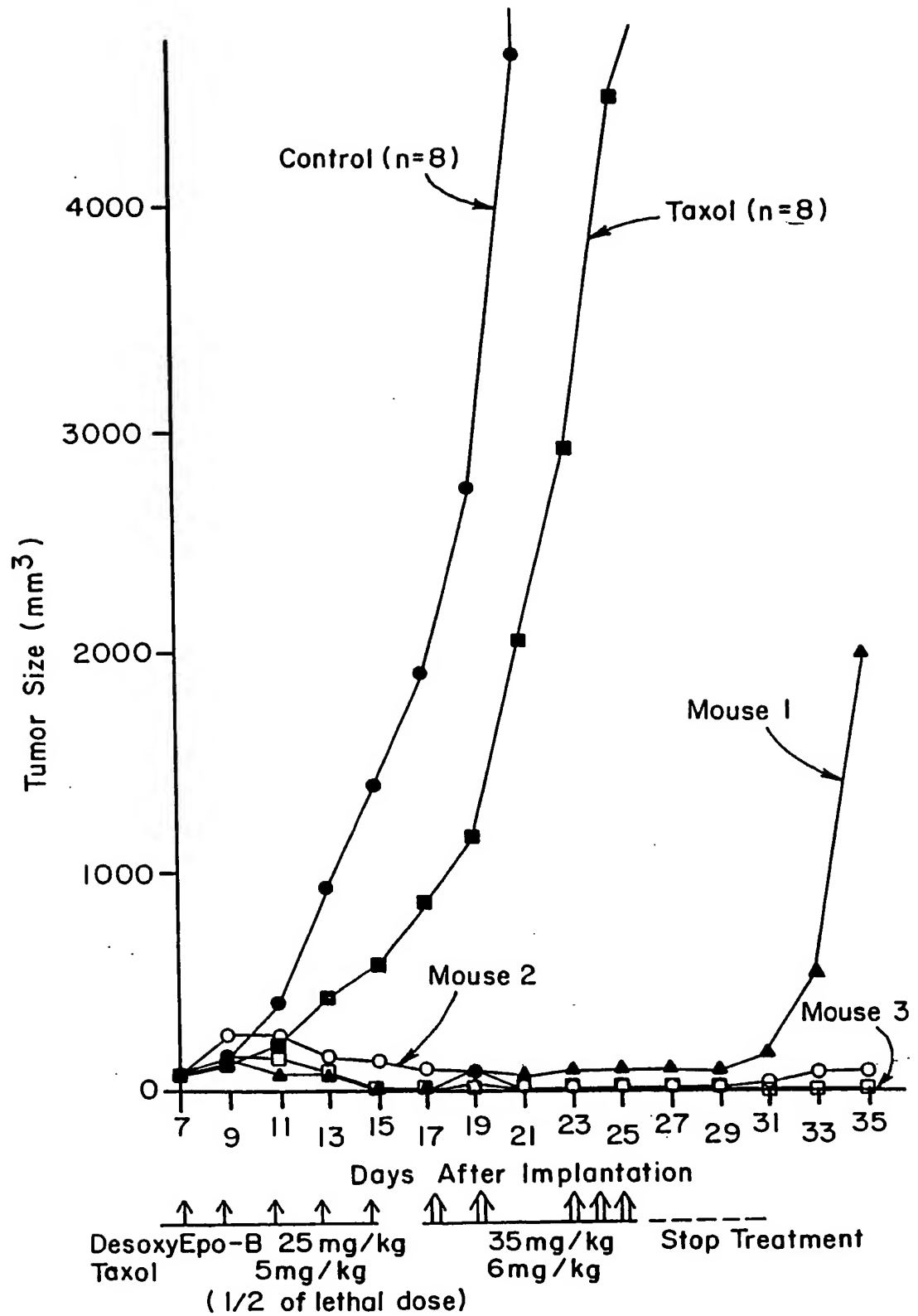
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FIG. 45A



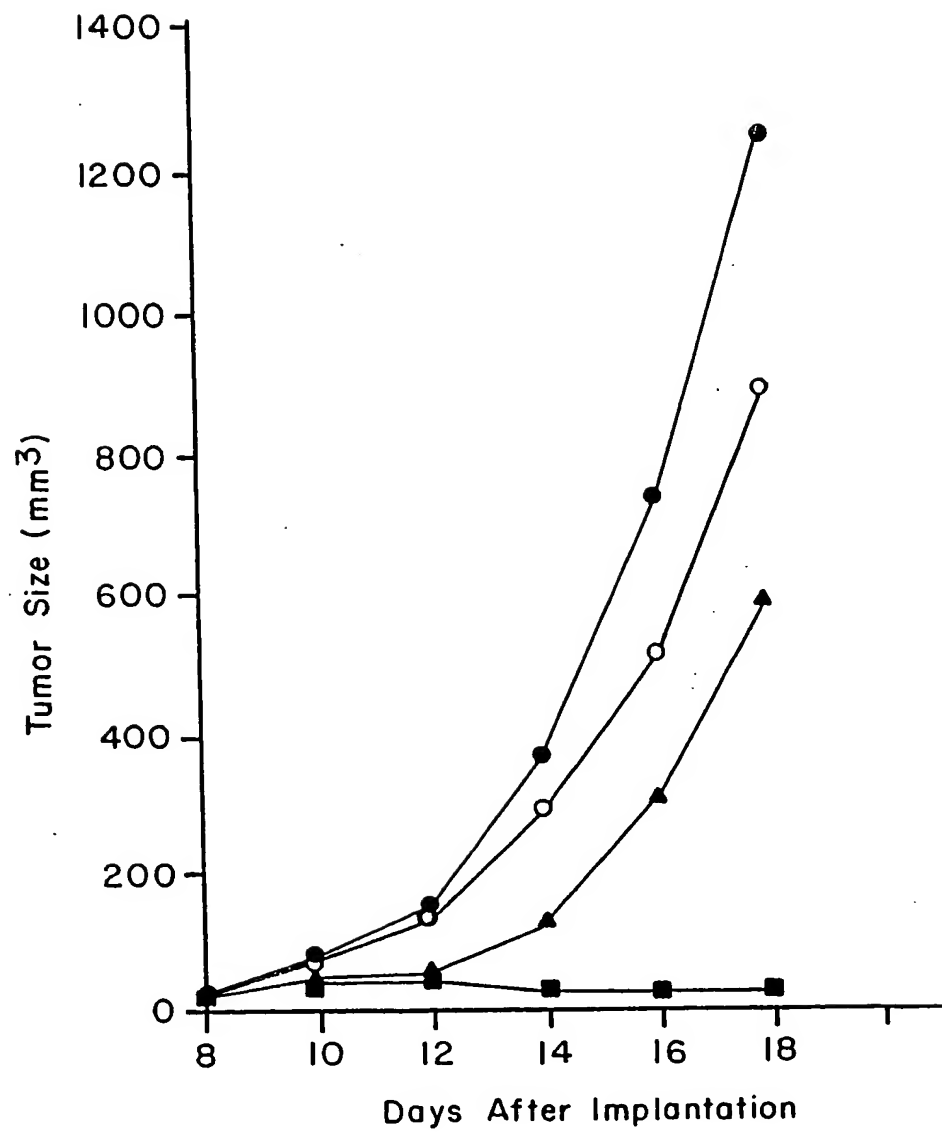
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FIG. 45 B



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FIG. 46



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FIG. 47

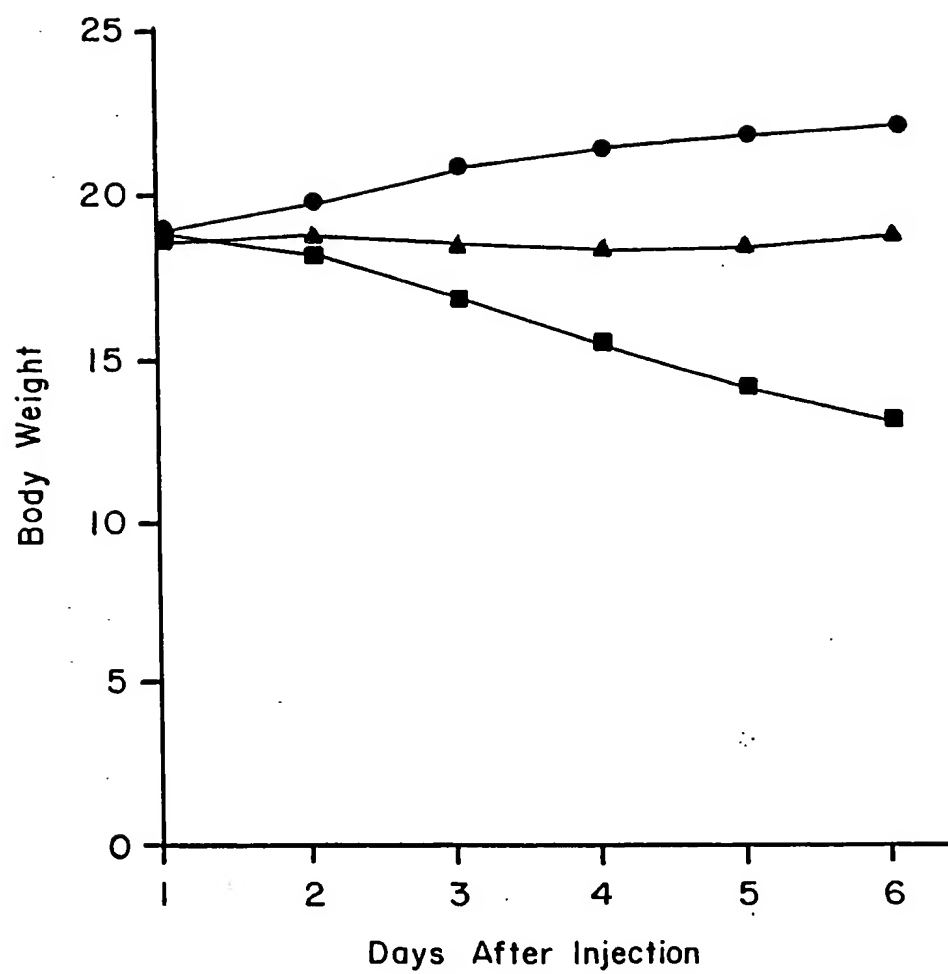
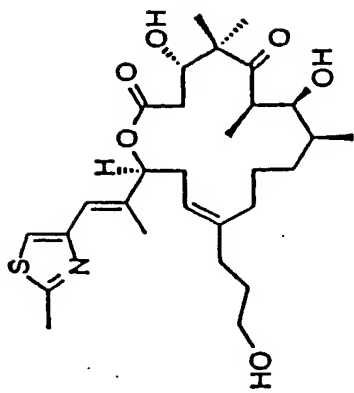
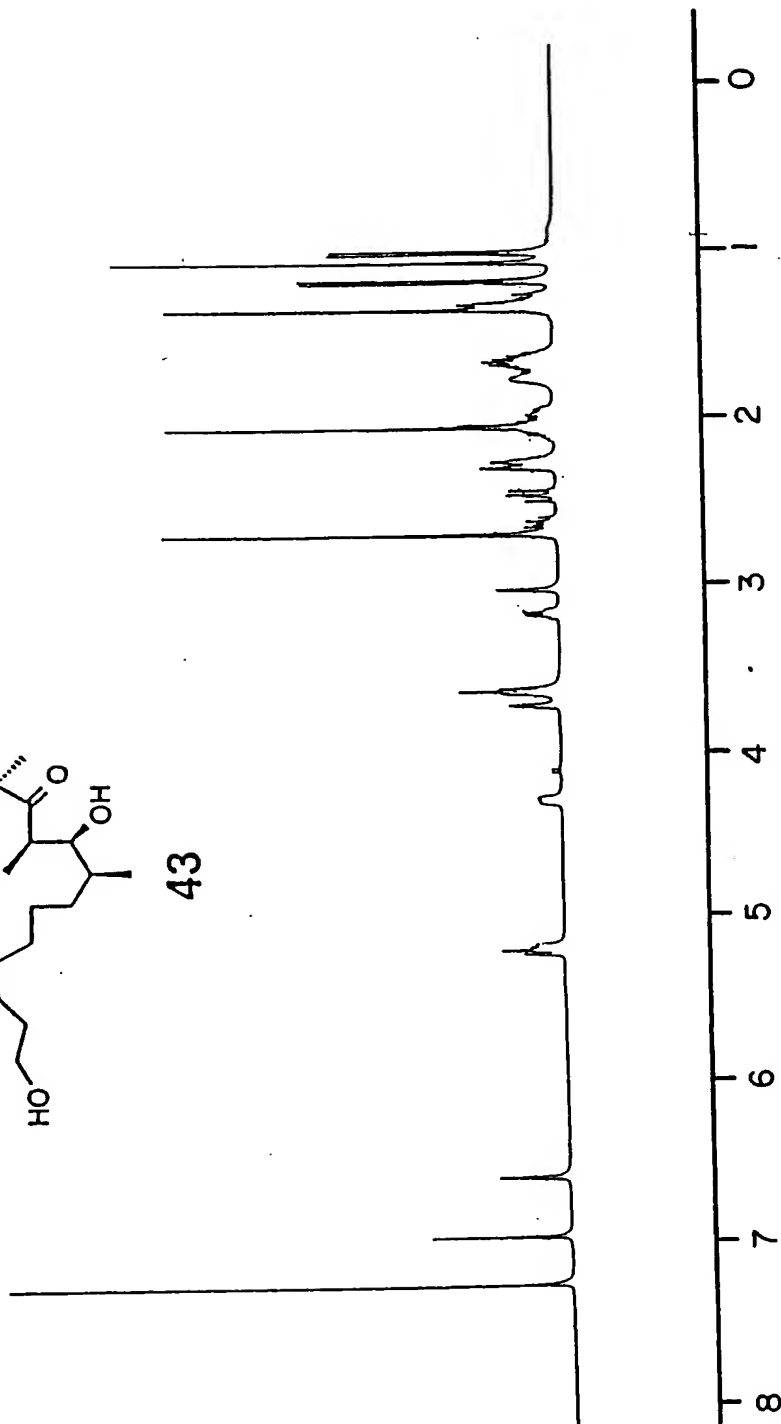


FIG. 48

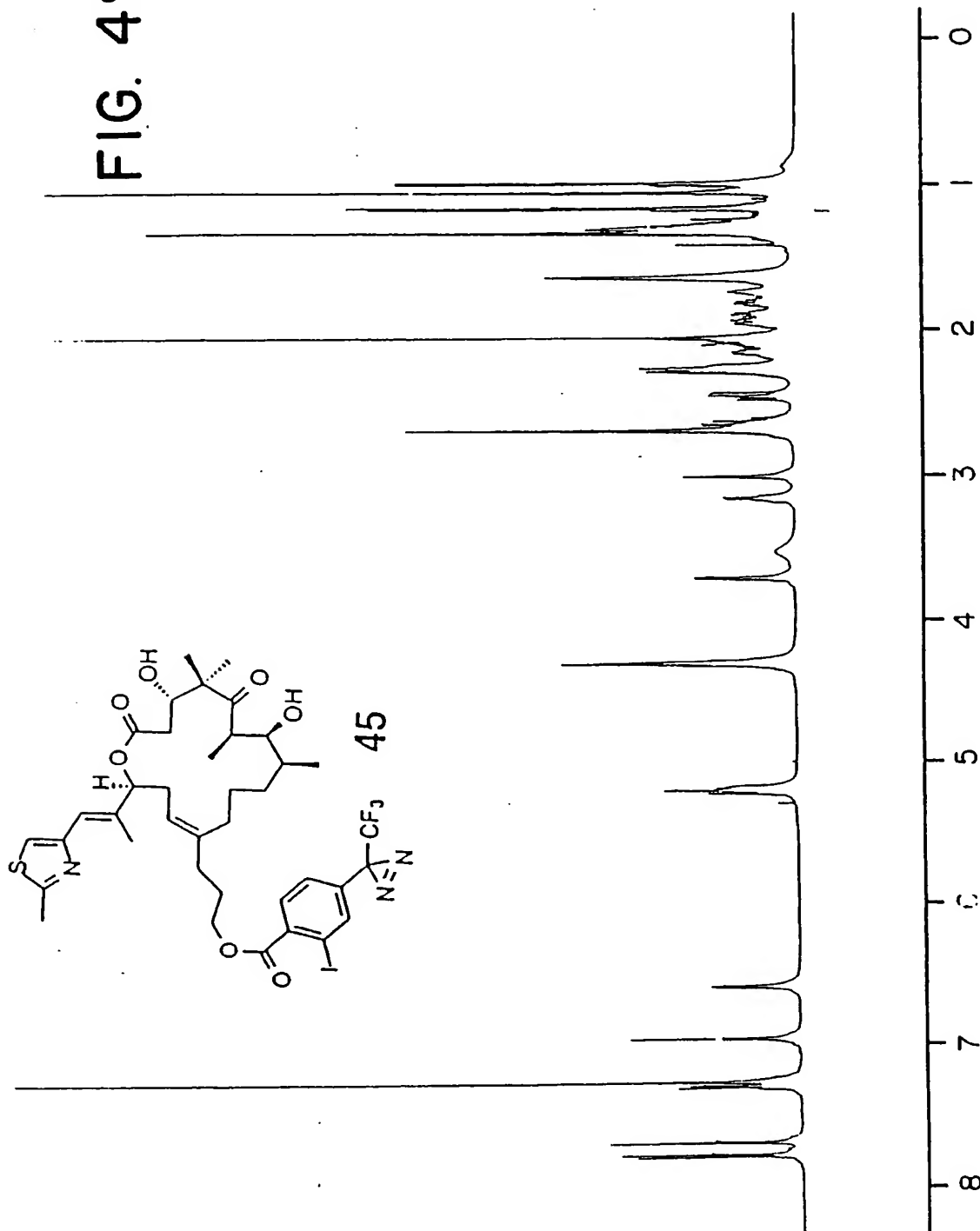


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FIG. 49



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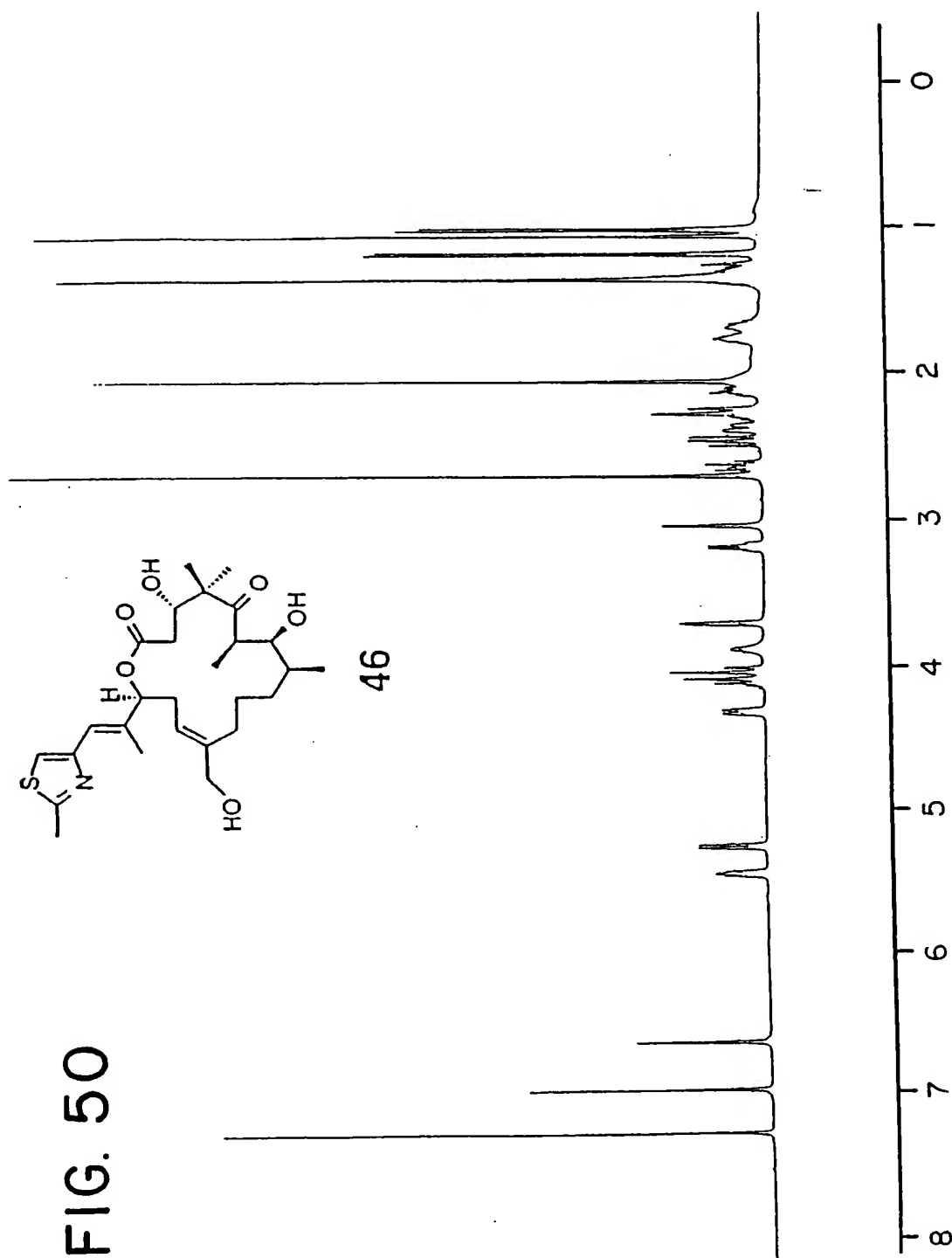
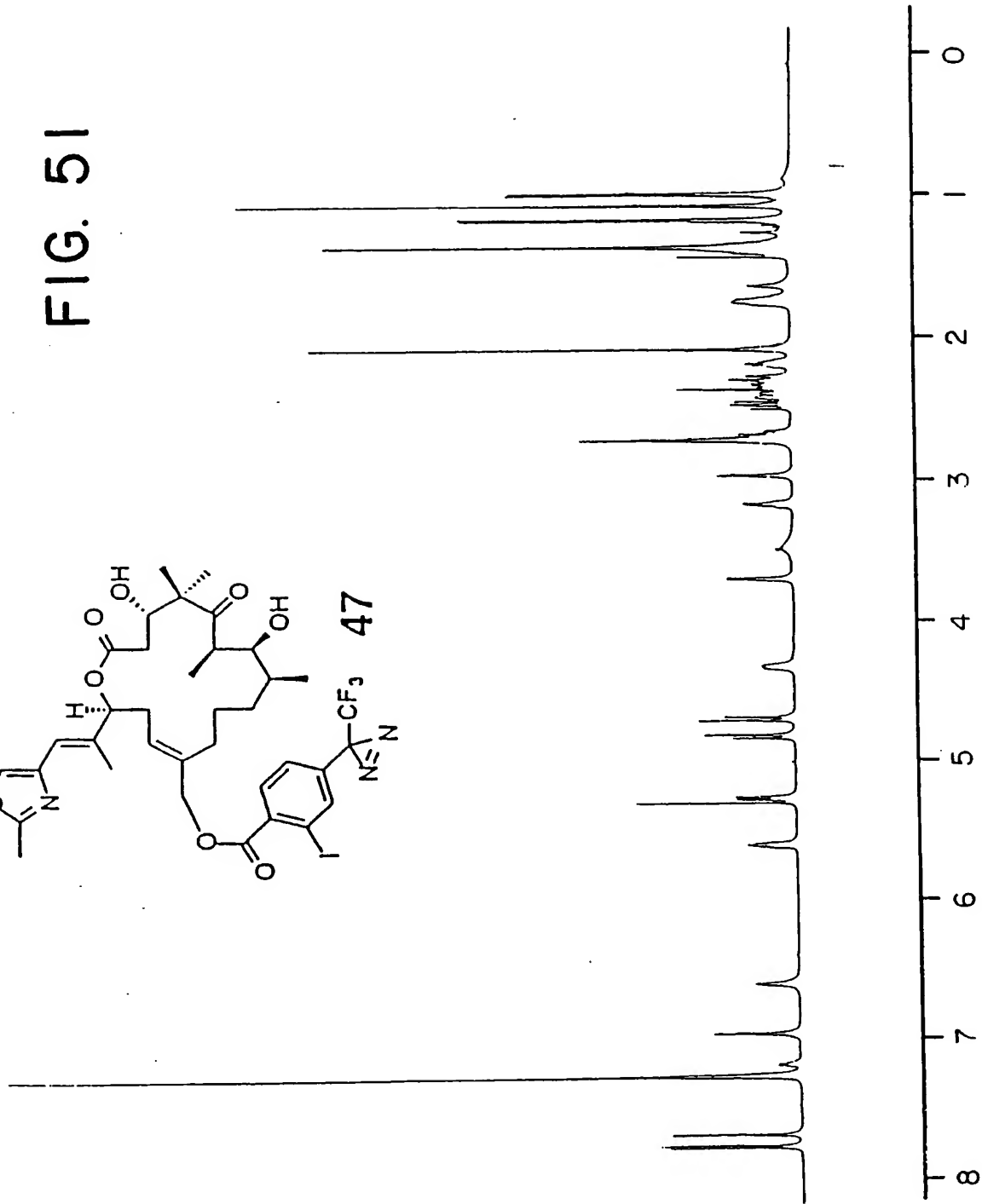
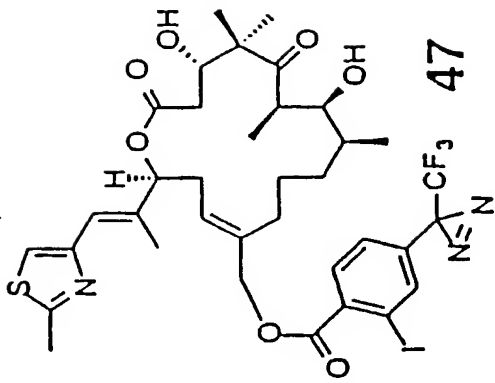


FIG. 15



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FIG. 52

